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**H A N D - B O O K**  
**OF**  
**C H E M I S T R Y.**

**BY**  
**LEOPOLD GMELIN.**

**VOL. XIII.**

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**ORGANIC CHEMISTRY,**  
**VOL. VII.**

**ORGANIC COMPOUNDS CONTAINING SIXTEEN AND EIGHTEEN ATOMS OF CARBON.**

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**TRANSLATED BY**  
**HENRY WATTS, B.A., F.C.S.**

**LONDON:**  
**PRINTED FOR THE CAVENDISH SOCIETY.**

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**MDCCCLIX.**

~~Chem 428.48.2~~

KPE 2575  
✓

1862, 8/12. 10.

LONDON:  
PRINTED BY HARRISON AND SONS,  
ST. MARTIN'S LANE, W.C.



# CONTENTS OF VOL. XIII.

(VOL. VII. OF ORGANIC CHEMISTRY.)

## COMPOUNDS CONTAINING 16 AT. CARBON.

### *Primary Nucleus C<sup>16</sup>H<sup>8</sup>.*

	Page
Styrol, C <sup>16</sup> H <sup>8</sup> ....	1
Metastyrol, C <sup>16</sup> H <sup>8</sup> ....	6
Toluylic acid, C <sup>16</sup> H <sup>8</sup> ,O <sup>4</sup> ....	8
Toluylates of Ammonia, Potash, Baryta, Copper, and Silver, C <sup>16</sup> H <sup>7</sup> MO <sup>4</sup> ....	9
Toluylate of Ethyl, C <sup>20</sup> H <sup>12</sup> O <sup>4</sup> = C <sup>4</sup> H <sup>6</sup> O,C <sup>16</sup> H <sup>7</sup> O <sup>3</sup> ....	10

### *Oxygen-nucleus C<sup>16</sup>H<sup>6</sup>O<sup>2</sup>.*

Phthalic acid, C <sup>16</sup> H <sup>6</sup> O <sup>8</sup> = C <sup>16</sup> H <sup>6</sup> O <sup>2</sup> ,O <sup>6</sup> ....	10
Phthalates, C <sup>16</sup> H <sup>6</sup> MO <sup>8</sup> and C <sup>16</sup> H <sup>4</sup> M <sup>2</sup> O <sup>8</sup> ....	12
Phthalate of Ammonia, C <sup>16</sup> H <sup>5</sup> (NH <sup>4</sup> )O <sup>8</sup> . — Phthalates of Potash and of Soda ....	12
Phthalates of Baryta, Lime, and Zinc ....	13
Phthalate of Lead, C <sup>16</sup> H <sup>4</sup> Pb <sup>2</sup> O <sup>8</sup> . — Phthalate of Silver, C <sup>16</sup> H <sup>4</sup> Ag <sup>2</sup> O <sup>8</sup> ....	13
Terephthalic acid, C <sup>16</sup> H <sup>8</sup> O <sup>8</sup> = C <sup>16</sup> H <sup>6</sup> O <sup>2</sup> ,O <sup>6</sup> ....	13
Terephthalate of Silver C <sup>16</sup> H <sup>4</sup> Ag <sup>2</sup> O <sup>8</sup> ....	14

### *Oxygen-nucleus C<sup>16</sup>H<sup>4</sup>O<sup>4</sup>.*

Phthalic Anhydride, C <sup>16</sup> H <sup>4</sup> O <sup>6</sup> = C <sup>16</sup> H <sup>4</sup> O <sup>4</sup> ,O <sup>2</sup> ....	14
--	----

### *Bromine-nucleus C<sup>16</sup>BrH<sup>7</sup>.*

Bromide of Styrol, C <sup>16</sup> Br <sup>2</sup> H <sup>8</sup> = C <sup>16</sup> BrH <sup>7</sup> ,HBr ....	15
--	----

### *Chlorine-nucleus C<sup>16</sup>ClH<sup>7</sup>.*

Chloryde of Styrol, C <sup>16</sup> Cl <sup>2</sup> H <sup>8</sup> = C <sup>16</sup> ClH <sup>7</sup> ,HCl ....	16
---	----

	Page
<i>Oxychlorine-nucleus</i> $C^{16}Cl^2H^4O^2$ .	
Bichlorophthalic acid, $C^{16}Cl^2H^4O^8 = C^{16}Cl^2H^4O^2, O^6$ ....	17
<i>Oxychlorine-nucleus</i> $C^{16}Cl^3H^3O^2$ .	
Terchlorophthalic acid, $C^{16}Cl^3H^3O^8 = C^{16}Cl^3H^3O^2, O^6$ ....	17
<i>Oxychlorine-nucleus</i> $C^{16}Cl^3HO^4$ .	
Terchlorophthalic Anhydride, $C^{16}Cl^3HO^8 = C^{16}Cl^3HO^4, O^2$ ....	18
<i>Nitro-nucleus</i> $C^{16}XH^7$ .	
Nitrostyrol, $C^{16}NH^7O^4 = C^{16}XH^7$ ....	18
Nitrometastyrol, $C^{16}NH^7O^4 = C^{16}XH^7$ ....	19
Nitrophthalin, $C^{16}NH^7O^4 = C^{16}XH^7$ ....	19
Phthalamine, $C^{16}NH^9O^4 = C^{16}XH^7, H^2$ ....	21
Ethyl-phthalamine, $C^{20}NH^{13}O^4 = C^{16}XH^6(C^4H^5), H^2$ ....	21
Nitrotoluylic acid, $C^{16}NH^7O^8 = C^{16}XH^7, O^4$ ....	22
Nitrotoluylates of Ammonia, Potash, Soda, Baryta, $C^{16}XH^6BaO^4$ , and Strontia ....	22
Nitrotoluylate of Lime, $C^{16}XH^6CaO^4$ . — Nitrotoluylate of Copper. — Nitrotoluylate of Silver, $C^{16}XH^6AgO^4$ ....	23
Nitrodraeylic acid, $C^{16}NH^7O^8 = C^{16}XH^7O^4?$ ....	23
Nitrotoluylate of Methyl, $C^{16}NH^9O^8 = C^2H^3O, C^{16}NH^6O^7$ ....	24
Nitrotoluylate of Ethyl, $C^{20}NH^{11}O^8 = C^4H^5O, C^{16}NH^6O^7$ ....	25
<i>Nitro-nucleus</i> $C^{16}X^3H^5$ .	
Nitrococcusic acid, $C^{16}N^3H^5O^{18} = C^{16}X^3H^5, O^6$ ....	25
Nitrococcusate of Ammonia, $C^{16}N^3H^3(NH^4)^2O^{18} + Aq$ ....	26
Nitrococcusate of Potash, $C^{16}N^3H^3K^2O^{18}$ . — Nitrococcusate of Baryta. — Nitrococcusate of Copper. — Nitrococcusate of Silver, $C^{16}N^3H^3Ag^2O^{18}$ ....	27
<i>Oxynitro-nucleus</i> $C^{16}XH^5O^2$ .	
Nitrophthalic acid, $C^{16}NH^5O^{12} = C^{16}XH^5O^2, O^6$ ....	27
Nitrophthalates, $C^{16}NH^4MO^{12}$ and $C^{16}NH^3M^2O^{12}$ ....	28
Nitrophthalates of Ammonia, $C^{16}NH^4(NH^4)O^{12}$ and $C^{16}NH^3(NH^4)^2O^{12}$ . — Nitrophthalate of Baryta, $C^{16}NH^3Ba^2O^{12}$ . — Nitrophthalate of Lead, $C^{16}NH^3Pb^2O^{12}, 2PbO$ . — Nitrophthalate of Silver, $C^{16}NH^3Ag^2O^{12}$ ....	29
<i>Oxyamidogen-nucleus</i> , $C^{16}AdH^5O^2$ .	
Phthalamic acid, $C^{16}NH^7O^6 = C^{16}AdH^5O^2, O^4$ ....	30
Phthalamate of Ammonia, $C^{16}NH^6(NH^4)O^6$ ....	30
Phenyl-phthalamic acid, $C^{28}NH^{11}O^6 = C^{16}NH^4(C^{12}H^5)O^6$ ....	31

	Page
Phthalimide, $C^{16}NH^5O^4 = C^{16}NH^5O^2, O^2$ ....	31
Silver-compound, $C^{16}NH^4AgO^4$ ....	32
Phenyl-phthalimide, $C^{20}NH^9O^4 = C^{16}NH^4(C^{12}H^5)O^2, O^2$ ....	32
Nitrophthalimide, $C^{16}N^2H^4O^8 = C^{16}XNH^4O^2, O^2$ ....	33

*Azo-nucleus  $C^{16}NH^7$ .*

Phthalidine, $C^{16}NH^9 = C^{16}NH^7, H^2$ ....	33
Sulphate, $C^{16}NH^9, HSO^4$ . — Hydrochlorate, $C^{16}NH^9, HCl$ . — Nitrate, $C^{16}NH^9, HNO^6$ ....	34
Ethylphthalidine, $C^{20}NH^{13} = C^{16}N(C^4H^5)H^6, H^2$ ....	35
Hydriodate. — Hydrochlorate, $C^{16}NH^{13}, HCl$ ....	35

*Azo-nucleus  $C^{16}NH^5O^2$ .*

Indigo-blue, $C^{16}NH^5O^2$ ....	35
<i>Appendix :</i>	
Indigo-red....	45
Colourless Indigo-red	47
Indigo-brown	48
Isatin, $C^{16}NH^5O^4 = C^{16}NH^5O^2, O^2$ ....	51
Metallic Isatides, $C^{16}NH^4MO^4$ ....	53
Isatides of Ammonium and Potassium. — Isatide of Cuprammonium, $C^{16}NH^4(NH^2Cu^2)O^4$ ....	53
Isatide of Silver, $C^{16}NH^4AgO^4$ ....	54
Isatide of Argentammonium, $C^{16}NH^4(NH^2Ag)O^4$ ....	54
Isatic acid, $C^{16}NH^7O^6 = C^{16}NH^7O^2, O^4$ ...	54
Isatate of Potash. — Isatate of Baryta, $C^{16}NH^6BaO^6$ . — Isatate of Silver, $C^{16}NH^6AgO^6$ ....	55
Isatosulphurous acid, $C^{16}NH^7S^2O^{10} = C^{16}NH^7O^6, 2SO^2$ ....	56
Isatosulphite of Ammonia, $C^{16}NH^6(NH^4)O^6, 2SO^2$ ....	56
Isatosulphite of Potash, $C^{16}NH^6KO^6, 2SO^2 + 5Aq$ ....	57

*Conjugated Compounds of the Nucleus  $C^{16}NH^5O^2$ .*

Sulphindigotic acid, $C^{16}NH^6S^2O^8 = C^{16}NH^5O^2, 2SO^3$ ....	58
Sulphindigotates : $C^{16}NH^4MO^2, 2SO^3$ ....	61
Sulphindigotate of Ammonia. — Sulphindigotate of Potash, $C^{16}NH^4KO^2, 2SO^3$ ....	62
Sulphindigotate of Soda. — Sulphindigotate of Baryta, $C^{16}NH^4BaO^2, 2SO^3$ ....	63
Sulphindigotates of Lime, Magnesia, Alumina, and Lead ...	64

*Appendix to Sulphindigotic Acid :*

Hyposulphindigotic acid	65
Sulphoviridic acid	66
Indigo-green	67
Sulphopurpuric acid	67

	Page
Sulphoflavic acid ....	68
Sulphofulvic and Sulphorufic acids ....	68
Indigo-yellow ....	68
<i>Oxybromazo-nucleus</i> $C^{16}NBrH^4O^2$ .	
Bromisatin, $C^{16}NBrH^4O^4 = C^{16}NBrH^4O^2, O^2$ ....	69
Bromisatic acid, $C^{16}NBrH^6O^6 = C^{16}NBrH^6O^2, O^4$ ....	70
<i>Oxybromazo-nucleus</i> $C^{16}NBr^2H^3O^2$ .	
Bibromisatin, $C^{16}NBr^2H^3O^4 = C^{16}NBr^2H^3O^2, O^2$ ....	70
Bibromisatic acid, $C^{16}NBr^2H^5O^6 = C^{16}NBr^2H^5O^2, O^4$ ....	71
Bibromisate of Potash, $C^{16}NBr^2H^4KO^6$ . — Bibromisates of Lead and Copper ....	71
Bibromisatate of Silver ....	72
Bibromisatosulphurous acid, $C^{16}NBr^2H^5S^2O^{10} = C^{16}NBr^2H^5O^6, 2SO^2$ ....	72
<i>Oxychlorazo-nucleus</i> $C^{16}NClH^4O^2$ .	
Chlorisatin, $C^{16}NClH^4O^4 = C^{16}NClH^4O^2, O^2$ ....	72
Chlorisatide of Potassium. — Chlorisatide of Silver. — Chlorisatide of Silver and Ammonium, $C^{16}NClH^2(NH^4)AgO^4$ ....	74
Chlorisatic acid, $C^{16}NClH^6O^6 = C^{16}NClH^6O^2, O^4$ ....	75
Chlorisatate of Potash, $C^{16}NClH^5KO^6$ ....	75
Chlorisatate of Baryta, $C^{16}NClH^5BaO^6$ : — also with Aq. and 3Aq. ....	76
Chlorisatate of Lead, $C^{16}NClH^5PbO^6 + 2Aq.$ ....	76
Chlorisatate of Silver, $C^{16}NClH^5AgO^6$ ....	77
Chlorisatosulphurous acid, $C^{16}NClH^6S^2O^{10} = C^{16}NClH^6O^6, 2SO^2$ ....	77
<i>Oxychlorazo-nucleus</i> $C^{16}NCl^2H^3O^2$ .	
Bichlorisatin, $C^{16}NCl^2H^3O^4 = C^{16}NCl^2H^3O^2, O^2$ ....	78
Bichlorisatic acid, $C^{16}NCl^2H^5O^6 = C^{16}NCl^2H^5O^2, O^4$ ....	79
Bichlorisatate of Potash, $C^{16}NCl^2H^4KO^6$ ....	80
Bichlorisatate of Baryta, $C^{16}NCl^2H^4BaO^6 + 2Aq$ ....	80
Bichlorisatate of Copper, $C^{16}NCl^2H^4CuO^6$ ....	81
Bichlorisatosulphurous acid, $C^{16}NCl^2H^5S^2O^{10} = C^{16}NCl^2H^5O^6, 2SO^2$ ....	81
<i>Oxyamidazo-nucleus</i> $C^{16}NAdH^4O^2$ .	
Imesatin, $C^{16}N^2H^6O^2 = C^{16}NAdH^4O^2$ ....	82
Phenylimesatin, $C^{28}N^2H^{10}O^2 = C^{16}N(C^{12}NH^6)H^4O^2$ ....	83
Bromophenylimesatin, $C^{28}N^2BrH^9O^2 = C^{16}N(C^{12}NBrH^5)H^4O^2$ ....	83
Chlorophenylimesatin, $C^{28}N^2ClH^9O^2 = C^{16}N(C^{12}NClH^5)H^4O^2$ ....	84
<i>Oxychloramidazo-nucleus</i> $C^{16}NAdClH^3O^2$ .	
Chlorimesatin, $C^{16}N^2ClH^5O^2 = C^{16}NAdClH^3O^2$ ....	85

*Conjugated Compounds containing 2 or more At. C<sup>16</sup>NH<sup>5</sup>O<sup>2</sup> or similar nuclei.*

Indin, C <sup>32</sup> N <sup>2</sup> H <sup>10</sup> O <sup>4</sup> (= 2 atoms of indigo-blue) ....	85
Indin-potassium, C <sup>32</sup> N <sup>2</sup> H <sup>9</sup> KO <sup>4</sup> ? ....	86
Bibromindin, C <sup>32</sup> N <sup>2</sup> Br <sup>4</sup> H <sup>6</sup> O <sup>4</sup> ....	87
Chlorindin, C <sup>32</sup> N <sup>2</sup> Cl <sup>2</sup> H <sup>8</sup> O <sup>4</sup> ....	87
Bichlorindin, C <sup>32</sup> N <sup>2</sup> Cl <sup>4</sup> H <sup>6</sup> O <sup>4</sup> ....	88
Nitrindin, C <sup>32</sup> N <sup>2</sup> X <sup>2</sup> H <sup>8</sup> O <sup>4</sup> ....	88
Hydrindin, C <sup>64</sup> N <sup>4</sup> H <sup>22</sup> O <sup>10</sup> = 2C <sup>32</sup> N <sup>2</sup> H <sup>10</sup> O <sup>4</sup> , H <sup>2</sup> O <sup>2</sup> ....	89
Potassium-compound, C <sup>64</sup> N <sup>4</sup> H <sup>21</sup> KO <sup>10</sup> + 6Aq ....	90
Flavindin, C <sup>48</sup> N <sup>3</sup> H <sup>16</sup> O <sup>6</sup> = 3C <sup>16</sup> NH <sup>5</sup> O <sup>2</sup> ....	91
Flavindic acid, C <sup>48</sup> N <sup>3</sup> H <sup>21</sup> O <sup>18</sup> = 3C <sup>16</sup> NH <sup>7</sup> O <sup>6</sup> ? ....	91
Indigo-white, C <sup>32</sup> N <sup>2</sup> H <sup>12</sup> O <sup>4</sup> = C <sup>32</sup> N <sup>2</sup> H <sup>10</sup> O <sup>4</sup> , H <sup>2</sup> ....	92
Sulphophœnicic acid, C <sup>32</sup> N <sup>2</sup> H <sup>10</sup> S <sup>2</sup> O <sup>10</sup> = C <sup>32</sup> N <sup>2</sup> H <sup>10</sup> O <sup>4</sup> , 2SO <sup>3</sup> ....	95
Ammonium-salt ....	96
Potassium-salt, C <sup>32</sup> N <sup>2</sup> H <sup>9</sup> KO <sup>4</sup> , 2SO <sup>3</sup> + 2Aq....	97
Isatan, C <sup>32</sup> N <sup>2</sup> H <sup>12</sup> O <sup>6</sup> ....	97
Isatyde, C <sup>32</sup> N <sup>2</sup> H <sup>12</sup> O <sup>8</sup> = 2C <sup>16</sup> NH <sup>5</sup> O <sup>4</sup> , H <sup>2</sup> ....	98
Bibromisatyde, C <sup>32</sup> N <sup>2</sup> Br <sup>4</sup> H <sup>8</sup> O <sup>8</sup> = C <sup>32</sup> N <sup>2</sup> Br <sup>4</sup> H <sup>6</sup> O <sup>8</sup> , H <sup>2</sup> ....	99
Chlorisatyde, C <sup>32</sup> N <sup>2</sup> Cl <sup>2</sup> H <sup>10</sup> O <sup>8</sup> = C <sup>32</sup> N <sup>2</sup> Cl <sup>2</sup> H <sup>8</sup> O <sup>8</sup> , H <sup>2</sup> ....	100
Chlorisatydic acid, C <sup>32</sup> N <sup>2</sup> Cl <sup>2</sup> H <sup>12</sup> O <sup>8</sup> ? ....	101
Sulphochlorisatin, C <sup>32</sup> N <sup>2</sup> Cl <sup>2</sup> H <sup>10</sup> S <sup>10</sup> or C <sup>32</sup> N <sup>2</sup> Cl <sup>2</sup> H <sup>10</sup> S <sup>8</sup> ? ....	101
Bichlorisatyde, C <sup>32</sup> N <sup>2</sup> Cl <sup>4</sup> H <sup>8</sup> O <sup>8</sup> = C <sup>32</sup> N <sup>2</sup> Cl <sup>4</sup> H <sup>6</sup> O <sup>8</sup> , H <sup>2</sup> ....	102
Bichlorisatydic acid, C <sup>32</sup> N <sup>2</sup> Cl <sup>4</sup> H <sup>10</sup> O <sup>8</sup> ....	103
Sulphisatyde, C <sup>32</sup> N <sup>2</sup> H <sup>10</sup> S <sup>2</sup> O <sup>6</sup> , H <sup>2</sup> or C <sup>32</sup> N <sup>2</sup> H <sup>10</sup> S <sup>2</sup> O <sup>4</sup> , 2HO ....	103
Bisulphisatanous acid, C <sup>32</sup> N <sup>2</sup> H <sup>10</sup> S <sup>4</sup> O <sup>4</sup> , H <sup>2</sup> or C <sup>32</sup> N <sup>2</sup> H <sup>10</sup> S <sup>2</sup> O <sup>4</sup> , 2HS ....	104
Sulphisatanous acid, C <sup>16</sup> NH <sup>7</sup> O <sup>4</sup> , 2SO <sup>3</sup> ? ....	105
Ammonium-salt, C <sup>16</sup> NH <sup>6</sup> (NH <sup>4</sup> )S <sup>2</sup> O <sup>8</sup> + 2Aq. ....	106
Imasatin, C <sup>32</sup> N <sup>3</sup> H <sup>11</sup> O <sup>6</sup> = C <sup>32</sup> N <sup>2</sup> AdH <sup>9</sup> O <sup>4</sup> , O <sup>2</sup> ? ....	106
Bibromimasatin, C <sup>32</sup> N <sup>2</sup> AdBr <sup>4</sup> H <sup>6</sup> O <sup>4</sup> , O <sup>2</sup> ....	108
Chlorimasatin, C <sup>32</sup> N <sup>2</sup> Cl <sup>2</sup> H <sup>9</sup> O <sup>6</sup> = C <sup>32</sup> N <sup>2</sup> AdCl <sup>2</sup> H <sup>7</sup> O <sup>4</sup> , O <sup>2</sup> ? ..	108
Isamic acid, C <sup>32</sup> N <sup>3</sup> H <sup>13</sup> O <sup>8</sup> = C <sup>32</sup> N <sup>2</sup> AdH <sup>11</sup> O <sup>4</sup> , O <sup>4</sup> ....	109
Isamates of Ammonia; Potash; Baryta, C <sup>32</sup> N <sup>3</sup> H <sup>12</sup> BaO <sup>8</sup> ....	110
Isamate of Silver, C <sup>32</sup> N <sup>3</sup> H <sup>12</sup> AgO <sup>8</sup> ....	111
Isamide, C <sup>32</sup> N <sup>4</sup> H <sup>14</sup> O <sup>6</sup> = C <sup>32</sup> N <sup>2</sup> Ad <sup>2</sup> H <sup>10</sup> O <sup>2</sup> , O <sup>4</sup> ....	111
Indelibrome, C <sup>32</sup> N <sup>3</sup> Br <sup>4</sup> H <sup>8</sup> O <sup>8</sup> ? ....	112
Chlorisamic acid, C <sup>32</sup> N <sup>3</sup> Cl <sup>2</sup> H <sup>11</sup> O <sup>8</sup> ....	112
Chlorisamide, C <sup>32</sup> N <sup>4</sup> Cl <sup>2</sup> H <sup>12</sup> O <sup>6</sup> ....	113
Bichlorisamic acid....	113
Bichlorisamide ...	114
Isatylim, C <sup>48</sup> N <sup>3</sup> AdH <sup>14</sup> O <sup>6</sup> , O <sup>4</sup> ? ....	114
Isatimide, C <sup>48</sup> N <sup>5</sup> H <sup>17</sup> O <sup>8</sup> = C <sup>48</sup> N <sup>3</sup> Ad <sup>2</sup> H <sup>13</sup> O <sup>6</sup> , O <sup>2</sup> ....	114
Amisatin, C <sup>96</sup> N <sup>11</sup> H <sup>39</sup> O <sup>10</sup> ....	115
Bibromocarmindin, C <sup>64</sup> N <sup>7</sup> Br <sup>8</sup> H <sup>15</sup> O <sup>10</sup> ...	116

	Page
<b>XYLENE SERIES.</b>	
<b>A. PRIMARY SERIES.</b>	
<i>Primary nucleus C<sup>18</sup>H<sup>10</sup>.</i>	
Xylol, C <sup>16</sup> H <sup>10</sup> ....	116
Sulphoxylic acid, C <sup>16</sup> H <sup>10</sup> S <sup>2</sup> O <sup>6</sup> = C <sup>16</sup> H <sup>10</sup> ,2SO <sup>3</sup> ....	117
Baryta-salt, C <sup>16</sup> H <sup>9</sup> BaS <sup>2</sup> O <sup>6</sup> ....	118
Terebentic acid, C <sup>16</sup> H <sup>10</sup> O <sup>4</sup> ....	118
Calcium-salt, C <sup>10</sup> H <sup>9</sup> CaO <sup>4</sup> . — Lead-salt. — Silver-salt, C <sup>16</sup> H <sup>9</sup> AgO <sup>4</sup> ....	119
<b>SECONDARY NUCLEI OF XYLENE.</b>	
<i>Oxygen-nucleus C<sup>16</sup>H<sup>8</sup>O<sup>2</sup>. Anisene.</i>	
Anisalcohol, C <sup>16</sup> H <sup>10</sup> O <sup>4</sup> = C <sup>16</sup> H <sup>8</sup> O <sup>2</sup> ,2HO ....	119
Anisylous acid, C <sup>16</sup> H <sup>8</sup> O <sup>4</sup> = C <sup>16</sup> H <sup>8</sup> O <sup>2</sup> ,O <sup>2</sup> ....	120
With Bisulphite of Ammonia. — With Bisulphite of Potash. — With	
Bisulphite of Soda, C <sup>18</sup> H <sup>10</sup> O <sup>4</sup> + NaO,2SO <sup>2</sup> + Aq. ....	122
Anisic acid, C <sup>16</sup> H <sup>8</sup> O <sup>6</sup> = C <sup>16</sup> H <sup>8</sup> O <sup>2</sup> ,O <sup>4</sup> ....	123
<i>Anisates</i> , C <sup>16</sup> H <sup>7</sup> MO <sup>6</sup> : Ammonium-salt, C <sup>16</sup> H <sup>7</sup> (NH <sup>4</sup> )O <sup>6</sup> . — Potassium-	
salt. — Barium-salt, C <sup>16</sup> H <sup>7</sup> BaO <sup>6</sup> + Aq. — Strontium-salt. —	
Calcium-salt ....	126
Lead-salt, C <sup>16</sup> H <sup>7</sup> PbO <sup>6</sup> . — Silver-salt, C <sup>16</sup> H <sup>7</sup> AgO <sup>6</sup> ....	127
Sulphanisic acid, C <sup>16</sup> H <sup>8</sup> S <sup>2</sup> O <sup>12</sup> = C <sup>16</sup> H <sup>8</sup> O <sup>6</sup> ,2SO <sup>3</sup> ....	128
Barium-salt, C <sup>16</sup> H <sup>6</sup> Ba <sup>2</sup> S <sup>2</sup> O <sup>12</sup> + 2Aq ....	128
Lead-salts: <i>Acid</i> , C <sup>16</sup> H <sup>7</sup> PbS <sup>2</sup> O <sup>12</sup> , — <i>Neutral</i> , C <sup>16</sup> H <sup>6</sup> Pb <sup>2</sup> S <sup>2</sup> O <sup>12</sup> + 2Aq. —	
Silver-salt ....	129
Anisate of Methyl, C <sup>18</sup> H <sup>10</sup> O <sup>6</sup> = C <sup>2</sup> H <sup>3</sup> O,C <sup>16</sup> H <sup>7</sup> O <sup>5</sup> ....	129
Anisate of Ethyl, C <sup>20</sup> H <sup>12</sup> O <sup>6</sup> = C <sup>4</sup> H <sup>5</sup> O,C <sup>16</sup> H <sup>7</sup> O <sup>5</sup> ....	130
Hydrochlorate of Anisene, C <sup>16</sup> H <sup>8</sup> O <sup>2</sup> ,HCl? ....	131
Thianisiol, C <sup>16</sup> H <sup>8</sup> O <sup>2</sup> ,S <sup>2</sup> ? ....	131
<i>Oxybromine-nucleus C<sup>16</sup>H<sup>7</sup>BrO<sup>2</sup>.</i>	
Bromide of Anisyl, C <sup>16</sup> H <sup>7</sup> BrO <sup>4</sup> = C <sup>16</sup> H <sup>7</sup> BrO <sup>2</sup> ,O <sup>2</sup> ....	132
Bromanisic acid, C <sup>16</sup> H <sup>7</sup> BrO <sup>2</sup> ,O <sup>4</sup> ....	132
Silver-salt, C <sup>16</sup> H <sup>6</sup> BrAgO <sup>6</sup> ....	133
Bromanisate of Methyl, C <sup>18</sup> H <sup>9</sup> BrO <sup>6</sup> = C <sup>2</sup> H <sup>3</sup> O,C <sup>16</sup> H <sup>6</sup> BrO <sup>5</sup> ...	133
Bromanisate of Ethyl, C <sup>20</sup> H <sup>11</sup> BrO <sup>6</sup> = C <sup>4</sup> H <sup>5</sup> O,C <sup>16</sup> H <sup>6</sup> BrO <sup>5</sup> ....	134
<i>Oxychlorine-nucleus C<sup>16</sup>H<sup>7</sup>ClO<sup>2</sup>.</i>	
Chloride of Anisyl, C <sup>16</sup> H <sup>7</sup> ClO <sup>4</sup> = C <sup>16</sup> H <sup>7</sup> ClO <sup>2</sup> ,O <sup>2</sup> ....	134
Chloranisic acid, C <sup>16</sup> H <sup>7</sup> ClO <sup>6</sup> = C <sup>16</sup> H <sup>7</sup> ClO <sup>2</sup> ,O <sup>4</sup> ....	135
Chloranisate of Methyl, C <sup>2</sup> H <sup>3</sup> O,C <sup>16</sup> H <sup>6</sup> ClO <sup>5</sup> ....	136
Chloranisate of Ethyl, C <sup>4</sup> H <sup>5</sup> O,C <sup>16</sup> H <sup>6</sup> ClO <sup>5</sup> ....	136
<i>Nitro-nucleus C<sup>16</sup>XH<sup>9</sup>.</i>	
Nitroxylol, C <sup>16</sup> NH <sup>9</sup> O <sup>4</sup> = C <sup>16</sup> XH <sup>9</sup> ....	137
Nitrosulphoxylic acid, C <sup>16</sup> XH <sup>9</sup> ,2SO <sup>3</sup> ....	137
Barium-salt, C <sup>16</sup> XH <sup>8</sup> Ba,2SO <sup>3</sup> ....	137

*Oxynitro-nucleus*  $C^{16}XH^7O^2$ .

Nitranisic acid, $C^{16}NH^7O^{10} = C^{16}XH^7O^2, O^4$ ....	137
Silver-salt, $C^{16}NH^6AgO^{10}$ ....	139
Nitranisate of Methyl, $C^2H^3O, C^{16}XH^6O^5$ ....	139
Nitranisate of Ethyl, $C^4H^5O, C^{16}XH^6O^5$ ....	140
Aniso-nitranisic acid, $C^{32}NH^{15}O^{16} = C^{16}XH^7O^6, C^{16}H^8O^6$ ....	140
Bromaniso-nitranisic acid, $C^{16}XH^7O^6, C^{16}BrH^7O^6$ ....	141
Chloraniso-nitranisic acid, $C^{16}XH^7O^6, C^{16}ClH^7O^6$ ....	142
Chloride of Nitranisyl, $C^{16}NClH^6O^8 = C^{16}ClXH^6O^4$ ....	142

*Oxynitro-nucleus*  $C^{16}X^3H^5O^2$ .

Ternitranisic acid, $C^{16}N^3H^5O^{18} = C^{16}X^3H^5O^2, O^4$ ....	143
--	-----

*Oxyamidogen-nucleus*  $C^{16}AdH^7O^2$ .

Anisamide, $C^{16}NH^9O^4 = C^{16}AdH^7O^2, O^2$ ....	143
Amidanisic acid, $C^{16}NH^9O^6 = C^{16}AdH^7O^2, O^4$ ....	143
Ammonium-salt. — Silver-salt, $C^{16}NH^8AgO^6$ ....	144
Chloroplatinate of Amidanisic acid, $C^{16}NH^9O^6, HCl, PtCl^2$ ....	145

*Conjugated compounds containing a nucleus derived from*  $C^{16}AdH^7O^2$ .

Anisanilide, $C^{28}NH^{13}O^4 = C^{16}(NH, C^{12}H^5)H^7O^2, O^2$ ....	145
Anishydramide, $C^{48}N^2H^{24}O^6 (= C^{48}AdNH^{22}O^6?)$ ....	145
Anisine, $C^{48}N^2H^{24}O^6 (= C^{48}N^2H^{22}O^6, H^2?)$ ....	146
Hydrochlorate, $C^{48}N^2H^{24}O^6, HCl$ . — Chloroplatinate, $C^{48}N^2H^{24}O^6, HCl, PtCl^2$ ....	146

*Azo-nucleus*  $C^{16}NH^9$ .

Xylidine, $C^{16}NH^{11} = C^{16}NH^9, H^2$ ....	147
Sulphate, $C^{16}NH^{11}, HSO^4$ . — Chloroplatinate, $C^{16}NH^{11}, HCl, PtCl^2$ ....	147
Collidine, $C^{16}NH^{11} = C^{16}NH^9, H^2$ ....	148
Chloroplatinate, $C^{16}NH^{11}, HCl, PtCl^2$ ....	149
Ethyl-collidine, $C^{20}NH^{15} = C^{16}N(C^4H^5)H^{10}$ ....	149
Chloroplatinate, $C^{20}NH^{15}, HCl, PtCl^2$ ....	150

*Primary nucleus*  $C^{16}H^{12}$ .*Oxygen-nucleus*  $C^{16}H^{10}O^2$ .

Beta-orcin, $C^{16}H^{10}O^2, O^2$ ....	150
---	-----

*Azo-nucleus*  $C^{16}NH^{11}$ .

Sparteine, $C^{16}NH^{13} = C^{16}NH^{11}, H^2$ ....	152
Chloromercurate, $C^{16}NH^{13}, HCl, HgCl$ ....	152
Chloroplatinate, $C^{16}NH^{13}, HCl, PtCl^2$ ....	153
Picrate, $C^{16}NH^{13}, C^{12}X^3H^3O^3$ ....	154



	Page
<i>Oxyazo-nucleus</i> $C^{16}NH^7O^4$ .	
Apophyllic acid, $C^{16}NH^7O^4, O^4$ ....	154
Hydrated Apophyllic acid ....	155
<i>Apophyllates</i> : Ammonium-salt ....	155
Barium-salt — Silver-salt, $C^{16}NH^6AgO^8$ ....	156
Apophyllo-nitrate of Silver, $C^{16}N^2H^6Ag^2O^{14}$ ....	156
<hr/>	
<i>Primary nucleus</i> $C^{16}H^{14}$ .	
<i>Oxygen-nucleus</i> $C^{16}H^{12}O^2$ .	
Camphrene, $C^{16}H^{12}O^2$ ....	156
<i>Oxygen-nucleus</i> , $C^{16}H^{10}O^4$ .	
Cholesteric acid, $C^{16}H^{10}O^4, O^4$ ....	157
Calcium-salt.—Silver-salt, $C^{16}H^8Ag^2O^8$ ....	159
<i>Azo-nucleus</i> $C^{16}NH^{13}$ .	
Conine, $C^{16}NH^{15} = C^{16}NH^{13}, H^2$ ....	159
Sulphate.—Hydrochlorate, $C^{16}NH^{15}, HCl$ ....	165
Nitrate.—Chloromercurate, $C^{16}NH^{15}, 4HgCl$ ....	166
Chloroplatinate, $C^{16}NH^{15}, HCl, PtCl^3$ ....	167
Conhydrine, $C^{16}NH^{17}O^2 = C^{16}NH^{15}, 2HO$ ....	169
Hydrochlorate.—Chloroplatinate, $C^{16}NH^{17}O^2, HCl, PtCl^3$ ....	169
<i>Conjugated Compounds containing a Nucleus derived from</i> $C^{16}H^{13}$ .	
Methylconine, $C^{18}NH^{17} = C^{16}N(C^2H^3)H^{12}, H^2$ ....	170
Ethylconine, $C^{20}NH^{19} = C^{16}N(C^4H^5)H^{12}, H^2$ ....	170
Hydriodate:—Hydrochlorate.—Chloroplatinate, $C^{20}NH^{19}, HCl, PtCl^3$ ....	171
Biethylconine, $C^{24}NH^{23} = C^{16}N(C^4H^5)^2H^{11}, H^2$ ....	172
Hydriodate.—Chloroaurate.—Chloroplatinate, $C^{24}NH^{23}, HCl, PtCl^3$ ....	173
Ethylmethylconine, $C^{22}NH^{21} = C^{16}N(C^2H^3)(C^4H^5)H^{11}, H^2$ ....	173
Carbonate:—Hydriodate, $C^{22}NH^{21}, HI$ ....	173
Chloromercurate, $C^{22}NH^{21}, HCl, 5HgCl$ and $C^{22}NH^{21}, HCl, 6HgCl$ ....	174
Chloroaurate, $C^{22}NH^{21}, HCl, AuCl^3$ .—Chloroplatinate, $C^{22}NH^{21}, HCl, PtCl^3$ ....	175
<hr/>	
<i>Primary nucleus</i> $C^{16}H^{16}$ .	
Oil of Wine, $C^{16}H^{16}$ ....	175
Etherin, $C^{16}H^{16}$ ....	176
<i>Appendix</i> : Sulphovinate of Wine-oil ....	177
Caprylene, $C^{16}H^{16}$ ....	180
Metacaprylene, $2C^{16}H^{16}?$ ....	182
Capryl, $C^{32}H^{24} = (C^{16}H^{16})^2, H^2$ ....	182
Caprylic Ether? $C^{16}H^{16}, HO$ ....	183

	Page
Caprylic Alcohol, $C^{16}H^{18}O^2 = C^{16}H^{16}, H^2O^2$ ....	183
Violet substance derived from Caprylic Alcohol, $C^{16}H^{15}ClNa^2?$ ....	186
Caprylic Aldehyde, $C^{16}H^{16}O^2$ ....	187
Sulphite of Caprylic Aldehyde and Potash, $C^{16}H^{16}O^2 + NaO, 2SO^2$ + 2Aq ....	188
<i>Appendix</i> : Methyl-œnanthol, $C^{16}H^{16}O^2 = C^2H^3O, C^{14}H^{13}O$ ....	189
Caprylic acid, $C^{16}H^{16}, O^4$ ....	190
Caprylates, $C^{16}H^{15}MO^4$ :	
Barium-salt, $C^{16}H^{15}BaO^4$ ....	192
Lead-salt, $C^{16}H^{15}PbO^4$ . — Silver-salt, $C^{16}H^{15}AgO^4$ ....	193
Sulphide of Capryl, $C^{16}H^{17}S = C^{16}H^{16}, HS$ ....	193
Iodide of Capryl, $C^{16}H^{17}I = C^{16}H^{16}, HI$ ....	193
Bromide of Capryl, $C^{16}H^{17}Br = C^{16}H^{16}, HBr$ ....	194
Chloride of Capryl, $C^{16}H^{17}Cl = C^{16}H^{16}, HCl$ ....	195

*Conjugated Compounds containing the Nucleus  $C^{16}H^{16}$ .*

Sulphocaprylic acid, $C^{16}H^{18}S^2O^8 = C^{16}H^{18}O^2, 2SO^8$ ....	196
Sulphocaprylates, $C^{16}H^{17}MS^2O^8$ .	
Potassium-salt, $C^{16}H^{17}KS^2O^8 + 2Aq$ . — Barium-salt, $C^{16}H^{17}BaS^2O^8$ + 3Aq. — Calcium-salt. — Lead-salts ....	197
Nitrate of Capryl, $C^{16}H^{17}NO^6 = C^{16}H^{17}O, NO^6$ ....	198
Methyl-caprylic ether, $C^2H^3O, C^{16}H^{17}O$ or Methyl-œnanthylic ether, $C^2H^3O, C^{14}H^{15}O$ ....	198
Caprylate of Methyl, $C^2H^3O, C^{16}H^{15}O^3?$ ....	199
Ethyl-caprylic ether, $C^4H^5O, C^{16}H^{17}O$ or Ethyl-œnanthylic ether, $C^4H^5O, C^{14}H^{15}O?$ ....	199
Acetate of Capryl, $C^{16}H^{17}O, C^4H^3O^8$ ....	200
Caprylone, $C^{20}H^{20}O^2 = C^{16}H^{16}O^2, C^{14}H^{14}$ ....	200
Caprylate of Ethyl, $C^4H^5O, C^{16}H^{15}O^3$ ....	201
Amyl-caprylic ether, $C^{10}H^{11}O, C^{16}H^{17}O$ or Amyl-œnanthylic ether, $C^{10}H^{11}O, C^{14}H^{15}O?$ ....	202
Caprylic Anhydride $(C^{16}H^{15}O^3)^2$ ....	202

*Oxygen-nucleus  $C^{16}H^{14}O^2$ .*

Hydride of Suberyl, $C^{16}H^{14}O^2$ ....	203
<i>Appendix</i> : Cork-resin ....	204
Suberic acid, $C^{16}H^{14}O^8 = C^{16}H^{14}O^2, O^6$ ....	204
Suberates, $C^{16}H^{12}M^2O^8$ ....	208
Ammonium-salt. — Potassium-salt. — Sodium-salt, $C^{16}H^{12}Na^2O^8$ ....	208
Barium-salt, $C^{16}H^{12}Ba^2O^8$ . — Strontium-salt, $C^{16}H^{12}Sr^2O^8$ . — Calcium- salt, $C^{16}H^{12}Ca^2O^8$ . — Magnesium-salt, $C^{16}H^{12}Mg^2O^8$ ....	209
Suberates of Aluminium, Uranium, Manganese, Zinc and Tin ....	210
Lead-salts, $C^{16}H^{12}Pb^2O^8$ and $C^{16}H^{12}Pb^2O^8, 4PbO$ ....	210
Ferrous and Ferric-salts. — Cobalt-salt. — Copper-salt, $C^{16}H^{12}Cu^2O^8$ .	
Mercurous-salt $C^{12}H^{12}O^6, 2Hg^2O$ . — Mercuric-salt....	211

	Page
Ammonio-mercurous and Ammonio-mercuric Suberates .....	212
Silver-salt, $C^{16}H^{12}Ag^2O^8$ ....	212
Suberate of Methyl, $C^{20}H^{18}O^6 = 2C^2H^3O, C^{16}H^{12}O^6$ ....	212
Suberate of Ethyl, $C^{24}H^{22}O^8 = 2C^4H^5O, C^{16}H^{12}O^6$ ....	213
Chlorosuberate of Ethyl, $C^{24}Cl^2H^{20}O^8$ ....	214
<i>Oxygen-nucleus <math>C^{16}H^{12}O^4</math>.</i>	
Aloisol, $C^{16}H^{12}O^6 = C^{16}H^{12}O^4, O^2 ?$ ....	214
Aloisic acid, $C^{16}H^{12}O^8 = C^{16}H^{12}O^4, O^4 ?$ ....	216
<i>Bromine-nucleus <math>C^{16}BrH^{15}</math>.</i>	
Hydrobromate of Bromocaprylene, $C^{16}Br^2H^{15} = C^{16}BrH^{15}, HBr$ ....	216
<i>Chlorine-nucleus <math>C^{16}ClH^{15}</math>.</i>	
Binoxide of Chlorocaprylene, $C^{16}ClH^{15}, O^3$ [or Chloride of Capryl, $C^{16}H^{15}O^2, Cl$ ] ....	216
<i>Chlorine-nucleus <math>C^{16}Cl^5H^{11}</math>.</i>	
Pentachlorocaprylene, $C^{16}Cl^5H^{11}$ ....	216
<i>Nitro-nucleus <math>C^{16}XH^{15}</math>.</i>	
Nitrocaprylene, $C^{16}NH^{15}O^4 = C^{16}XH^{15}$ ....	217
Nitrocaprylic acid, $C^{16}NH^{15}O^8 = C^{16}XH^{15}, O^4$ ....	217
Silver-salt, $C^{16}XH^{14}Ag, O^4$ ....	218
Nitrocaprylate of Ethyl, $C^{20}NH^{19}O^8 = C^4H^5O, C^{16}XH^{14}O^3$ ....	218
<i>Nitro-nucleus <math>C^{16}X^2H^{14}</math>.</i>	
Binitrocaprylene, $C^{16}N^2H^{14}O^8 = C^{16}X^2H^{14}$ ....	219
<i>Amidogen-nucleus <math>C^{16}AdH^{15}</math>.</i>	
Caprylamine, $C^{16}NH^{19} = C^{16}AdH^{15}, H^2$ ....	219
Sulphate, $C^{16}NH^{19}, HSO^4$ . — Hydriodate, $C^{16}NH^{19}, HI$ . — Hydrochlorate, $C^{16}NH^{19}, HCl$ ....	220
Nitrate, $C^{16}NH^{19}, HNO^6$ . — Gold-salt, $C^{16}NH^{19}, HCl, AuCl^3$ . — Platinum-salt, $C^{16}NH^{19}, HCl, PtCl^2$ ....	221
<i>Oxyamidogen-nucleus <math>C^{16}AdH^{15}O^2</math>.</i>	
Suberamic acid, $C^{16}NH^{15}O^6 = C^{16}AdH^{13}O^2, O^4$ ....	221
<i>Oxyamidogen-nucleus <math>C^{16}Ad^2H^{12}O^2</math>.</i>	
Suberamide, $C^{16}N^2H^{16}O^4 = C^{16}Ad^2H^{12}O^2, O^2$ ....	221
Suberanilic acid, $C^{28}NH^{19}O^6 = C^{16}(C^{12}NH^6)H^{12}O^2, O^4$ ....	222
Suberanilide, $C^{40}N^2H^{24}O^4 = C^{16}(C^{12}NH^6)^2H^{12}O^2, O^2$ ....	223

*Oxyazo-nucleus*  $C^{16}N^4H^8O^4$ .

Caffeine, $C^{16}N^4H^{10}O^4 = C^{16}N^4H^8O^4, H^2$ ....	223
Hydrate of Caffeine, $C^{16}N^4H^{10}O^4 + 2Aq$ ....	231
Sulphate of Caffeine ....	231
Hydrochlorate, $C^{16}N^4H^{10}O^4, HCl$ and $C^{16}N^4H^{10}O^4, 2HCl$ . — Nitrate. —	
Caffeine with Nitrate of Silver, $C^{16}N^4H^{10}O^4, AgNO^6$ ....	232
Caffeine with Chloride of Mercury, $C^{16}N^4H^{10}O^4, 2HgCl$ ....	233
Chloroaurate of Caffeine, $C^{16}N^4H^{10}O^4, HCl, AuCl^3$ ....	233
Chloroplatinate of Caffeine, $C^{16}N^4H^{10}O^4, HCl, PtCl^2$ ....	234
Caffeine with Cyanide of Mercury, $C^{16}N^4H^{10}O^4, 2HgCy$ ....	234
Tannate of Caffeine ....	235

*Oxychlorazo-nucleus*  $C^{16}N^4ClH^7O^4$ .

Chlorocaffeine, $C^{16}N^4ClH^7O^4, H^2$ ....	235
---	-----

*Cyanazo-nucleus*  $C^{16}CyN^2H^{13}$ .

Cyanethine, $C^{16}N^3H^{15} = C^{16}CyN^2H^{13}, H^2$ ....	236
Nitrate, $C^{16}N^3H^{15}, HNO^6$ . — Chloroplatinate, $C^{16}N^3H^{15}, HCl, PtCl^2$ ....	236
Acetate. — Oxalate. — Tetrachloromethylsulphite....	237

*Primary-nucleus*  $C^{16}H^{18}$ .*Oxygen-nucleus*  $C^{16}H^{12}O^6$ .

Glucic acid, $C^{16}H^{12}O^6, O^6$ ....	237
Calcium-salts, $C^{16}H^{10}Ca^2O^{12} + Aq$ and $C^{16}H^{11}CaO^{12}$ . — Lead-salt, $C^{16}H^{10}Pb^2O^{12}, 2PbO$ ....	239

*Oxygen-nucleus*  $C^{16}H^{10}O^8$ .

Jelly from Pine-needles, $C^{16}H^{10}O^8, O^2$ ....	239
Appendix: Jelly from Pine-bark and <i>Thuja occidentalis</i> , $C^{16}H^{12}O^4$ or $C^{16}H^{10}O^{12}$ ? ....	240

*Appendix to Anisene.*

Anisic Anhydride, $C^{16}H^7O^5, C^{16}H^7O^5$ ....	241
Anisuric acid, $C^{20}H^{11}NO^8 = C^{20}AdH^9O^8$ ....	241
Anisosalicyl, $C^{16}H^7O^5, C^{14}H^5O^3$ ....	242

*Appendix to Vol. XII, p. 246.*

Acetosalicyl, $C^4H^3O^3, C^{14}H^5O^3$ ....	242
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## COMPOUNDS CONTAINING 18 AT. CARBON.

*Primary-nucleus C<sup>18</sup>H<sup>6</sup>. — Azo-nucleus C<sup>16</sup>NH<sup>5</sup>.*

Chinoline, C <sup>18</sup> NH <sup>7</sup> = C <sup>18</sup> NH <sup>5</sup> ,H <sup>2</sup> ....	243
Monohydrated Chinoline, C <sup>16</sup> NH <sup>7</sup> + Aq ....	247
Terhydrated Chinoline, C <sup>16</sup> NH <sup>7</sup> + 3Aq ....	248
Sulphate of Chinoline. — Hydrochlorate ....	248
Nitrate. — Chromate, C <sup>18</sup> NH <sup>7</sup> ,HO,2CrO <sup>3</sup> ....	249
Chloride of Uranyl with Hydrochlorate of Chinoline, C <sup>18</sup> NH <sup>7</sup> ,HCl + U <sup>2</sup> O <sup>2</sup> Cl ....	249
Chloride of Cadmium with Hydrochlorate of Chinoline, C <sup>18</sup> NH <sup>7</sup> ,HCl + 2CdCl ....	250
Chloride of Mercury with Chinoline, C <sup>18</sup> NH <sup>7</sup> ,2HgCl....	250
Chloroaurate of Chinoline, C <sup>18</sup> NH <sup>7</sup> ,HCl,AuCl <sup>3</sup> ....	250
Chloroplatinate of Chinoline, C <sup>18</sup> NH <sup>7</sup> ,HCl,PtCl <sup>3</sup> ....	251
Chloropalladite of Chinoline, C <sup>18</sup> NH <sup>7</sup> ,HCl,PdCl. — Oxalate of Chinoline ....	251
Picrate and Formate of Chinoline ....	252

*Conjugated Compounds containing the nucleus C<sup>18</sup>NH<sup>5</sup>.*

Methylchinoline, C <sup>20</sup> NH <sup>9</sup> = C <sup>18</sup> N(C <sup>2</sup> H <sup>3</sup> )H <sup>4</sup> ,H <sup>2</sup> ...	252
Appendix: Methyloiridine ....	253
Ethylchinoline, C <sup>22</sup> NH <sup>11</sup> = C <sup>18</sup> N(C <sup>4</sup> H <sup>5</sup> )H <sup>4</sup> ,H <sup>2</sup> ....	254
Appendix: Ethyloiridine ....	255
Amylchinoline, C <sup>26</sup> NH <sup>17</sup> = C <sup>18</sup> N(C <sup>10</sup> H <sup>11</sup> )H <sup>4</sup> ,H <sup>2</sup> ....	255

*Primary-nucleus C<sup>18</sup>H<sup>8</sup>.*

Styrone, C <sup>18</sup> H <sup>10</sup> O <sup>2</sup> = C <sup>18</sup> H <sup>8</sup> ,H <sup>2</sup> O <sup>2</sup> ....	256
Cinnamic Aldehyde, C <sup>18</sup> H <sup>8</sup> ,O <sup>2</sup> ....	258
Hydrochlorate, C <sup>18</sup> H <sup>8</sup> O <sup>2</sup> ,HCl. — Nitrate, C <sup>18</sup> H <sup>8</sup> O <sup>2</sup> ,NO <sup>5</sup> ....	262
Compounds with Alkaline Bisulphites ....	263
Resins from Oil of Cinnamon ....	264
Compound of Iodine, Iodide of Potassium, and Oil of Cinnamon ....	267
Cinnamic acid, C <sup>18</sup> H <sup>8</sup> ,O <sup>4</sup> ....	268
Cinnamates, C <sup>18</sup> H <sup>7</sup> MO <sup>4</sup> ....	273
Ammonium-salt, C <sup>18</sup> H <sup>7</sup> (NH <sup>4</sup> )O <sup>4</sup> . — Potassium-salt, C <sup>18</sup> N <sup>7</sup> KO <sup>4</sup> + Aq. — Sodium-salt, C <sup>18</sup> H <sup>7</sup> NaO <sup>4</sup> + Aq. ....	274
Barium-salt, C <sup>18</sup> H <sup>7</sup> BaO <sup>4</sup> + 2Aq. — Strontium-salt. — Calcium-salt, C <sup>18</sup> H <sup>7</sup> CaO <sup>4</sup> + 2Aq. — Magnesium-salt. — Cerous and Lanthanous salts. — Glucinum and Aluminium salts....	275
Manganous, Antimonious, Zinc, and Cadmium salts. — Lead-salt, C <sup>18</sup> H <sup>7</sup> PbO <sup>4</sup> . — Iron-salts ....	276
Cobalt, Copper, and Mercurous salts ....	277
Silver-salts: α. Acid? — β. Neutral, C <sup>18</sup> H <sup>7</sup> AgO <sup>4</sup> ....	277

# CONTENTS.

xvii

	Page
Thiocinol, $C^{18}H^8S^2$ ....	278
Sulphocinnamic acid, $C^{18}H^8O^4, 2SO^3$ ....	278
Sulphocinnamates : — Neutral, $C^{18}H^6M^2O^4, 2SO^3$ . — Acid, $C^{18}H^7MO^4, 2SO^3$ ....	279
Potassium-salt, $C^{18}H^6K^2O^4, 2SO^3 + Aq.$ ....	279
Barium-salts, $C^{18}H^6Ba^2O^4, 2SO^3 + 2Aq.$ and $C^{18}H^7BaO^4, 2SO^3 + 2Aq.$	280
Barium-ammonium-salt — Zinc and Copper salts — Silver-salt, $C^{18}H^6Ag^2O^4, 2SO^3$ ....	280
Cinnamate of Methyl, $C^2H^3O, C^{18}H^7O^3$ ....	281
Cinnamate of Ethyl, $C^4H^5O, C^{18}H^7O^3$ ....	281
Cinnamein, $C^{20}H^{14}O^4 = C^{14}H^7O, C^{18}H^{17}O^3$ ....	283
Styracin, $C^{26}H^{16}O^4 = C^{18}H^9O, C^{18}H^7O^3$ ....	286
<i>Appendix.</i> — Cinnamate of Styracin ....	289
Myroxocarpin, $C^{48}H^{26}O^6?$ ...	289
Resins from Tolu-balsam ....	290
Cinnamic Anhydride, $C^{18}H^7O^3, C^{18}H^7O^3$ ....	292
Aceto-cinnamic Anhydride, $C^4H^3O^3, C^{18}H^7O^3$ ....	293
Benzo-cinnamic Anhydride, $C^{14}H^5O^3, C^{18}H^7O^3$ ....	293

## *Iodine-nucleus* $C^{18}IH^7$ .

Iodocinnamic acid, $C^{18}IH^7, O^4?$ ....	293
--	-----

## *Bromine-nucleus* $C^{18}BrH^7$ .

Bromocinnamic acid, $C^{18}BrH^7, O^4$ ....	294
---	-----

## *Chlorine-nucleus* $C^{18}ClH^7$ .

Chloride of Cinnamyl, $C^{18}ClH^7, O^3$ ....	294
Chlorocinnamic acid, $C^{18}ClH^7, O^4$ ....	295
Ammonium-salt, $C^{18}Cl(NH^4)H^6O^4 + Aq.$ —Potassium-salt.—Barium- salt, $C^{18}ClH^6BaO^4 + Aq.$ — Calcium-salt. — Silver-salt, $C^{18}ClH^6AgO^4$ ....	296
Chlorinated Oil from Cinnamic acid ....	297

## *Chlorine-nucleus* $C^{18}Cl^4H^4$ .

Tetrachlorocinnamyl, $C^{18}Cl^4H^4, O^3$ ....	298
Chlorostyracin, $C^{26}Cl^4H^{12}O^4 = C^{18}Cl^4H^5O, C^{18}H^7O^3?$ ....	299

## *Cyanogen-nucleus* $C^{18}CyH^7$ .

Cyanide of Cinnamyl, $C^{20}NH^7O^3 = C^{18}CyH^7, O^3$ ....	299
--	-----

## *Nitro-nucleus* $C^{18}XH^7$ .

Nitrocinnamic acid, $C^{18}NH^7O^3 = C^{18}XH^7, O^4$ ....	300
Ammonium, Potassium, and Magnesium salts. — Silver-salt, $C^{18}XH^6AgO^4$ ....	301

	Page
Nitrocinnamate of Ethyl, $C^{22}NH^{11}O^3 = C^4H^6O, C^{18}XH^6O^3$ ....	301
Nitrocinnamic Anhydride, $C^{36}N^2H^{12}O^{14} = (C^{18}XH^6O^3)^2$ ....	302

*Oxyamidogen-nucleus,  $C^{18}AdH^5O^3$ .*

Carbostyryl, $C^{18}NH^7O^2 = C^{18}AdH^5O^3$ ....	302
--	-----

*Conjugated Compounds containing  $C^{18}H^8$ , or a derived nucleus.*

Cinnanilide, $C^{30}NH^{13}O^3 = C^{18}Ad(C^{12}H^5)H^6, O^3$ ....	303
Cinnanitransidine, $C^{32}N^2H^{14}O^3 = C^{14}AdXH^5O, C^{18}H^7O^3$ ....	304
Hydrocinnamide, $C^{54}N^2H^{21} = C^{64}AdNH^{22}?$ ....	304
Triphenylamine or Bicinnamylamine, $C^{36}NH^{15} = C^{18}N(C^{18}H^7)H^6, H^3$ ....	305
Hydrochlorate ...	305
Chloromercurate. — Bicinnamylamine with Bichloride of Platinum, $C^{36}NH^{15}, PtCl^2$ . — Chloroplatinate, $C^{36}NH^{15}, HCl, PtCl^2$ . — Oxalate ....	306
Ethylbicinnamylamine, $C^{40}NH^{19} = C^{18}N(C^4H^5)(C^{18}H^7)H^5, H^3$ ....	307

*Primary Nucleus  $C^{18}H^{10}$ .*

Phloretic acid, $C^{18}H^{10}, O^6$ ....	307
Phloretates : — Neutral, $C^{18}H^9M^2O^6$ . — Acid, $C^{18}H^9MO^6$ ....	309
Potassium-salt, $C^{18}H^9KO^6$ . — Sodium-salt, $C^{18}H^9NaO^6$ ....	310
Barium-salts, $C^{18}H^9Ba^2O^6 + Aq.$ and $+ 5Aq$ ; and $C^{18}H^9BaO^6$ ....	310
Calcium and Magnesium salts. — Zinc-salts : neutral ? and acid, $C^{18}H^9ZnO^6$ . — Lead-salts, $C^{18}H^9Pb^2O^6 + Aq$ and $C^{18}H^9O^4, 3PbO + 2Aq$ ....	311
Copper-salts, $C^{18}H^9Cu^2O^6$ and $C^{18}H^9CuO^6$ . — Mercury-salts — Silver-salt, $C^{18}H^9AgO^6$ ....	312
Phloretate of Urea, $2C^{18}H^{10}O^6, C^2N^2H^4O^2$ ....	313
Sulphophloretic acid, $C^{18}H^{10}S^2O^{12} = C^{18}H^{10}O^6, 2SO^3$ ....	313
Sodium-salt, $C^{18}H^9Na^2O^6, 2SO^3$ ....	313
Barium-salt, $C^{18}H^9Ba^2O^6, 2SO^3 + 6Aq$ . — Calcium-salt, $C^{18}H^9Ca^2O^6, 2SO^3 + 8Aq$ . — Magnesium-salt, $C^{18}H^9Mg^2O^6, 2SO^3 + 4Aq$ ....	314
Ethylphloretic acid, $C^{22}H^{14}O^6 = C^4H^6O^2, C^{18}H^8O^4$ ....	314
Amylphloretic acid, $C^{28}H^{20}O^6 = C^{10}H^{12}O^2, C^{18}H^8O^4$ ....	315

*Appendix to Phloretic acid.*

Phloretol, $C^{18}H^{10}, O^2$ ....	316
Ternitrophloretol, $C^{16}X^3H^7, O^3$ ....	317

*Oxygen-nucleus  $C^{18}H^8O^3$ .*

Cumario acid, $C^{18}H^8O^3, O^4$ ....	317
Silver-salt, $C^{18}H^7AgO^6$ ....	318



	Page
Insolinic acid, $C^{18}H^8O^2, O^6$ ....	318
Potassium-salts, $C^{18}H^6K^2O^8$ and $C^{18}H^7KO^8$ ....	320
Insolinate of Potassium and Sodium, $C^{18}H^6KNaO^8$ ....	320
Barium-salt, $C^{18}H^6Ba^2O^8$ . — Calcium-salt, $C^{18}H^6Ca^2O^8$ . — Copper-salt, $C^{18}Cu^2H^6O^8 + CuO, HO?$ ....	320
Silver-salt, $C^{18}H^6Ag^2O^8$ ....	321

*Oxygen-nucleus  $C^{18}H^6O^4$ .*

Cumarin, $C^{18}H^6O^4$ ....	321
Combination with Tetrachloride of Antimony, $C^{18}H^7O^4, SbCl^3 ?$ ....	325
Purpurin, $C^{18}H^6O^4, O^2$ ....	325

*Bromine-nucleus  $C^{18}Br^2H^8$ .*

Bibromophloretic acid, $C^{18}Br^2H^8, O^6$ ....	330
Ammonium-salt — Barium-salt, $C^{18}Br^2H^7BaO^6$ ....	331

*Nitro-nucleus  $C^{18}X^2H^8$ .*

Binitrophloretic acid, $C^{18}N^2H^8O^{14} = C^{18}X^2H^8, O^6$ ....	331
Ammonium-salt, $C^{18}X^2H^6(NH^4)^2O^6$ ....	332
Potassium-salt, $C^{18}X^2H^6K^2O^6$ . — Barium-salt, $C^{18}X^2H^6Ba^2O^6$ . — Calcium-salt ....	333
Ethylbinitrophloretic acid, $C^4H^6O^2, C^{18}X^2H^6O^4$ ....	333

*Oxynitro-nucleus  $C^{18}XH^5O^4$ .*

Nitrocumarin, $C^{18}NH^5O^8 = C^{18}XH^5O^4$ ....	334
Lead-compound, $C^{18}XH^5O^4, 3PbO$ . — Silver-compound, $C^{18}XH^5O^4, 2AgO$ ....	335

*Amidogen-nucleus,  $C^{18}AdH^9$ .*

Phloretamic acid, $C^{18}NH^{11}O^4 = C^{18}AdH^9, O^4$ ....	335
--	-----

*Azo-nucleus,  $C^{18}NH^9$ .*

Cinchonidine, $C^{18}NH^{10}O = C^{18}NH^9, HO$ ....	336
--	-----

*Oxyazo-nucleus  $C^{18}NH^5O^4$ .*

Cumaramine, $C^{18}NH^7O^4 = C^{18}NH^5O^4, H^2$ ....	337
Hydrochlorate. — Chloroplatinate, $C^{18}NH^7O^4, HCl, PtCl^3$ ....	338

*Primary Nucleus  $C^{18}H^{12}$ .*

Cumene or Cumol, $C^{18}H^{12}$ ....	338
Mesitylene or Mesitylol, $C^{18}H^{12}$ (see vol. ix, p. 17)	
Methol, $C^{18}H^{12}$ (ix, 47)	
Hydrocarbon, $C^{18}H^{12}$ ....	341
Phorone, $C^{18}H^{14}O^2 = C^{18}H^{12}, 2HO$ ....	342

	Page
Bihydrate of Mesitylene, $C^{18}H^{12}, 2HO$ ....	343
Chloride of Phoryl, $C^{18}ClH^{12} = C^{18}H^{12}, HCl$ ....	343
Sulphocumolic acid, $C^{18}H^{12}, 2SO^3$ ....	344
Barium-salt, $C^{18}H^{11}Ba, 2SO^3$ ....	344
Mesityl-sulphuric acid (ix, 30).	
<i>Oxygen-nucleus <math>C^{18}H^6O^6</math>.</i>	
Bergaptene, $C^{18}H^6O^6 ?$ ....	345
<i>Bromine-nucleus <math>C^{18}Br^3H^9</math>.</i>	
Terbromomesitylene, $C^{18}Br^3H^9$ (ix, 19).	
<i>Chlorine-nucleus <math>C^{18}Cl^3H^{10}</math>.</i>	
Oil from Thymol, $C^{18}Cl^3H^{10}$ ....	346
<i>Nitro-nucleus <math>C^{18}XH^{11}</math>.</i>	
Nitrocumol, $C^{18}NH^{11}O^4 = C^{18}XH^{11}$ ....	347
Nitromesitylol, $C^{18}XH^{11}$ (ix, 20).	
<i>Nitro-nucleus <math>C^{18}X^2H^{10}</math>.</i>	
Binitrocumol, $C^{18}N^2H^{10}O^3 = C^{18}X^2H^{10}$ ....	347
Binitromesitylol, $C^{18}X^2H^{10}$ (ix, 20).	
<i>Nitro-nucleus <math>C^{18}X^3H^9</math>.</i>	
Ternitromesitylol, $C^{18}X^3H^9$ (ix, 21).	
<i>Azo-nucleus <math>C^{18}NH^{11}</math>.</i>	
Cumidine, $C^{18}NH^{12} = C^{18}NH^{11}, H^2$ ....	348
Phosphate. — Sulphate, $C^{18}NH^{12}, HSO^4$ ....	349
Hydriodate. — Hydrobromate. — Hydrochlorate, $C^{18}NH^{12}, HCl$ . —	
Hydrofluante. — Nitrate, $C^{18}NH^{12}, HNO^6$ ....	850
Chloroplatinate, $C^{18}NH^{12}, HCl, PtCl^2$ . — Palladium-salt. — Oxalate	351
Parvoline, $C^{18}NH^{12} = C^{18}NH^{11}, H^2$ ....	351
<i>Oxynitro-nucleus <math>C^{18}N^2H^6O^4</math>.</i>	
Acid from Naphthylamine, $C^{18}N^2H^6O^4, O^4$ ....	352
<i>Nitrazo-nucleus <math>C^{18}NXH^{10}</math>.</i>	
Nitrocumidine, $C^{18}N^2H^{12}O^4 = C^{18}NXH^{10}, H^2$ ....	852
Nitromesidine, $C^{18}NXH^{10}, H^2$ (ix, 21).	
Conjugated Compound : Cyanocumidine, $C^{40}N^4H^{26} = C^{36}Cy^2Ad^2H^{20}, H^2$	353
<hr/>	
<i>Primary Nucleus <math>C^{18}H^{14}</math>.</i>	
<i>Oxygen-nucleus <math>C^{18}H^{10}O^4</math>.</i>	
Veratric acid, $C^{18}H^{10}O^4, O^4$ ....	354
Silver-salt, $C^{18}H^9Ag^2O^3$ ....	355

# CONTENTS.

xxi

	Page
Veratrate of Ethyl, $C^4H^6O, C^{18}H^9O^7$ ....	355

## *Oxynitro-nucleus, $C^{18}XH^9O^4$ .*

Nitroveratric acid, $C^{18}XH^9O^4, O^4$ ....	356
---	-----

## *Appendix to Veratric Acid.*

Veratrol, $C^{16}H^{10}O^3, O^2$ ....	356
Binitroveratrol, $C^{16}X^2H^8O^4$ ....	357
Bibromoveratrol, $C^{16}Br^2H^8O^4$ ....	357

## *Oxyamidogen-nucleus $C^{18}AdH^7O^6$ .*

Tyrosine, $C^{18}NH^{11}O^6 = C^{18}AdH^7O^6, H^2$ ....	358
Hydrochlorate of Tyrosine, $C^{18}NH^{11}O^6, HCl$ ....	361
Tyrosine-sulphuric acid ....	362

## *Oxyamidonitro-nucleus $C^{18}AdXH^6O^6$ .*

Nitrotyrosine, $C^{18}N^3H^{10}O^{10} = C^{18}AdXH^6O^6, H^2$ ....	363
Sulphate. — Hydrochlorate. — Nitrate, $C^{18}N^2H^{10}O^6, HNO^6$ ....	363
Silver-compound of Nitrotyrosine, $C^{18}NH^9AgO^{10} + C^{18}NH^8Ag^2O^{10}$ ....	364

## *Azo-nucleus $C^{18}N^4H^{10}$ .*

Hydrocyanaldine, $C^{18}N^4H^{10}, H^2$ ....	364
--	-----

## *Primary Nucleus $C^{18}H^{16}$ .*

Campholene, $C^{18}H^{16}$ ....	365
---------------------------------	-----

## *Oxygen-nucleus $C^{18}H^{10}O^6$ .*

Apoglucic acid, $C^{18}H^{10}O^6, O^4$ ....	365
Calcium-salt, $C^{18}H^9CaO^{10}$ .—Lead-salt, $C^{18}H^9PbO^{10}$ ....	366
Silver-salt, $C^{18}H^9AgO^{10}$ ....	367

## *Primary Nucleus $C^{18}H^{18}$ .*

Pelargonene, $C^{18}H^{18}$ ....	367
Napththene, $C^{18}H^{18}$ ....	36
Bichloride of Pelargone, $C^{18}H^{18}Cl^2$ ....	368
Pelargonic acid, $C^{18}H^{18}, O^4$ ....	369
Pelargonate of Ammonia; of Potash; of Lime; of Baryta, $C^{18}H^{17}BaO^4$ ; of Strontia ....	370
Pelargonate of Copper, $C^{18}H^{17}CuO^4 + 2Aq$ : of Silver, $C^{18}H^{17}AgO^4$	371

	Page
Nitrosopelargonic acid, $C^{15}N^2H^{18}O^8 = C^{18}H^{18}O^4, 2NO^2$ ....	371
Nitrosopelargonate of Ammonia; of Potash; of Soda; of Baryta, $C^{18}H^{17}BaO^4, 2NO^2$ ; of Silver, $C^{18}H^{17}AgO^4, 2NO^2$ ....	372
Pelargonate of Ethyl, $C^4H^5O, C^{18}H^{17}O^3$ ....	372
Pelargonic Anhydride, $C^{18}H^{17}O^3, C^{18}H^{17}O^3$ ....	373
Benzo-pelargonic Anhydride. $C^{14}H^6O^3, C^{18}H^{17}O^3$ ....	373
Pelargone, $C^{34}H^{34}O^2 = C^{18}H^{18}O^2, C^{16}H^{16}$ ....	374

*Oxygen-nucleus  $C^{18}H^{16}O^3$ .*

Anchoic acid, $C^{18}H^{16}O^3 = C^{18}H^{16}O^2, O^1$ ....	374
Anchoates :—Neutral, $C^{18}H^{14}M^2O^5$ .—Acid, $C^{18}H^{16}MO^3$ ....	375
Anchoate of Ethyl, $2C^4H^5O, C^{18}H^{14}O^5$ ....	376

*Oxygen-nucleus  $C^{18}H^{14}O^4$ .*

Crotonol, $C^{18}H^{14}O^4$ ....	377
----------------------------------	-----

*Chlorine-nucleus  $C^{18}ClH^7$ .*

Chloride of Pelargyl, $C^{18}ClH^{17}O^2$ ....	377
--	-----

*Azo-nucleus  $C^{18}N^2H^{16}$ .*

Acetonine, $C^{18}N^2H^{16}, H^2$ ....	378
Chloroplatinate, $C^{18}N^2H^{16}, HCl, PtCl^2$ .—Oxalate $C^{16}N^2H^{18}, C^4H^2O^8 + 2Aq$ ....	378
<i>Appendix.</i> —Thiacetonine, $C^{18}NH^{19}S^4$ ....	378
Carbothiacetonine, $C^{20}N^2H^{18}S^4$ ....	379

*Primary Nucleus  $C^{18}H^{20}$ .*

*Oxysulphi-nucleus  $C^{18}(SO^2)^2H^{16}O^2$ .*

Sulphocamphoric acid, $C^{18}H^{16}S^2O^{12} = C^{18}(SO^2)^2H^{16}O^2, O^6 ?$ ....	379
Sulphocamphorate of Ammonia, $C^{18}H^{14}(NH^4)^2S^2O^{12} + 2Aq$ ; of Potash, $C^{18}H^{14}K^2S^2O^{12}$ ; of Baryta, $C^{18}H^{14}Ba^2S^2O^{12}$ ....	379
Sulphocamphorate of Lime, $C^{18}H^{14}Ca^2S^2O^{12}$ ; of Lead, $C^{18}H^{14}Pb^2S^2O^{12}$ ; of Copper; of Barium and Copper ....	380
Sulphocamphorate of Silver, $C^{18}H^{14}Ag^2S^2O^{12}$ ....	383

## ADDITIONS TO VOL. VII.

	Page
<b>Action of Potash and Soda on Organic Compounds :</b>	
Formation of Oxalates ....	385
Formation of Cyanides ....	386
Alcohol-radicals from Boghead Cannel Coal ....	386
Volatile Organic Bases and Fatty Acids (natural occurrence) ....	387
Action of Alkaline Hydrates on Compound Ethers ....	388
Bioxymethylene ( $C^2H^2, O^2$ ) <sup>2</sup> ....	389
Iodide of Methylene $C^2H^2I^2$ ....	390
Chloride and Bromide of Methylene ....	391
Acetate of Methylene, $C^2H^2, (C^4H^2O^2)^2, O^4$ ....	392
Chloride of Methyl ....	393
Bimethylamine ( $C^2H^3$ ) <sup>2</sup> , H, N ....	393
Bimethyl-biethylammonium, ( $C^2H^3$ ) <sup>2</sup> , ( $C^4H^5$ ) <sup>2</sup> N ....	394
Trimethylamine ....	395
<b>Mercury-compounds of Tetramethylum</b>	
a. ( $C^2H^3$ ) <sup>4</sup> Ni + 2HgI ....	395
b. ( $C^2H^3$ ) <sup>4</sup> Ni + 3HgI ....	396
Zinc-methyl ....	397
Mercuric Methyl, $C^2H^3Hg$ ....	398
Nitrate of Mercurous Methyl, $C^2H^3Hg^2, NO^6$ ....	399
Iodoform. — Sulphoform, $C^2HS^2$ ? ....	399
Chloroform ....	400
Urea ....	401
Compounds of Urea with Chlorides ....	403
Compounds of Urea with Organic acids ....	405
Cyanogen (formation) ....	407
Protocyanide of Iron ....	407
Ferrocyanide of Potassium. — Ferrocyanide of Aluminium, $3FeCy,$ $2Al^2Cy^3$ ....	408
Decomposition of Cyanides by Hydriodic Ethers ....	408

## ADDITIONS TO VOL. VIII.

Cuprosoferrocyanide of Potassium, $3KCy, 2Cu^2Cy, 2FeCy$ ....	409
Cyanide of Mercury (compounds of) ....	409
Cyanide of Silver (compounds of) ....	410
Cyanide of Methyl with Chlorides ....	411
Sulphocyanides. — Nitroprussides ....	413
Hydride of Ethyl; its coefficients of absorption in water ....	414
Ethylated Sulphuric acid ....	414
Alcohol : its preparation ....	414
Decomposition by the Electric Spark ....	415
Decomposition by Aqua regia ....	416
Etherification ....	416
Action of Hydrochloric acid upon Alcohol ....	416

	Page
Action of Hydriodic and Hydrobromic acid upon Alcohol. — Action of Mercuric Oxide on Bromide and Iodide of Ethyl ....	417
Action of Water on Bromide and Iodide of Ethyl; of Bromide and Iodide of Ethyl upon Alcohol; of Metallic Chlorides, Bromides, and Iodides upon Alcohol ....	418
Action of Sulphuric acid and Sulphates upon Alcohol ....	419
Formation of Oil of Wine, &c. ....	420
Ethylate of Sodium ....	420
Action of Alcoholic Potash on Chlorine-compounds ....	421
Alcoholate of Baryta, $\text{BaO}, \text{C}^4\text{H}^6\text{O}^2?$ ....	422
Glycol and its derivatives ....	422
Preparation and Oxidation of Glycol ....	422
Action of $\text{PCl}^5$ and of $\text{ZnCl}$ on Glycol ....	423
Action of $\text{SbCl}^3$ and of $\text{Na}$ on Glycol ....	424
Glycolic Ethers	
Oxide of Ethylene, $\text{C}^4\text{H}^4, \text{O}^2$ ....	424
Intermediate Glycol-ether, $(\text{C}^4\text{H}^4)^2, \text{H}^2, \text{O}^6$ ....	426
Ethyl-Glycol, $\left. \begin{array}{l} \text{C}^4\text{H}^4 \\ \text{C}^4\text{H}^5, \text{H} \end{array} \right\} \text{O}^4$ ....	426
Biethyl-glycol, $\text{C}^4\text{H}^4(\text{C}^4\text{H}^5)^2, \text{O}^4$ ....	427
Glycolic Chlorhydrin, $\text{C}^4\text{H}^4, \text{HO}^2, \text{Cl}$ ....	427
Glycolic Bromhydrin and Glycolic Iodhydrin ....	428
Sulphoglycolic acid, $\text{C}^4\text{H}^4\text{O}^2, 2\text{SO}^4\text{H}$ ....	428
Monoacetate of Ethylene, $\left. \begin{array}{l} \text{C}^4\text{H}^4 \\ \text{C}^4\text{H}^3\text{O}^2, \text{H} \end{array} \right\} \text{O}^4$ ....	429
Biacetate of Ethylene, $\left. \begin{array}{l} \text{C}^4\text{H}^4 \\ (\text{C}^4\text{H}^3\text{O}^2)^2 \end{array} \right\} \text{O}^4$ ....	430
Basic Acetate of Ethylene, $\text{C}^4\text{H}^4(\text{C}^4\text{H}^3\text{O}^2)^2, \text{O}^6?$ ....	430
Glycolic Chloracetin, $\text{C}^4\text{H}^4, \text{C}^4\text{H}^3\text{O}^4, \text{Cl}$ ....	430
Glycolic Iodacetin, $\text{C}^4\text{H}^4, \text{C}^4\text{H}^3\text{O}^4, \text{I}$ ....	431
Oxalate of Ethylene, $\text{C}^4(\text{C}^4\text{H}^4)\text{O}^8$ ....	432
Bibutyrate of Ethylene $\text{C}^4\text{H}^4(\text{C}^8\text{H}^7\text{O}^2)^2\text{O}^4$ ...	432
Glycolic Chlorobutyryn, $\text{C}^4\text{H}^4, \text{C}^8\text{H}^7\text{O}^4, \text{Cl}$ ....	432
Acetobutyrate of Ethylene, $\text{C}^4\text{H}^4, \text{C}^4\text{H}^3\text{O}^4, \text{C}^8\text{H}^7\text{O}^4$ ....	433
Bibenzoate of Ethylene $\text{C}^4\text{H}^4(\text{C}^{14}\text{H}^5\text{O}^2)^2\text{O}^4$ ....	433
Bistearate of Ethylene, $\text{C}^4\text{H}^4(\text{C}^{36}\text{H}^{36}\text{O}^2)\text{O}^4$ ....	434
Glyoxylic acid, $\text{C}^4\text{H}^2\text{O}^6$ ....	434
Glycolic acid, $\text{C}^4\text{H}^4\text{O}^6$ ....	435
Aldehyde	
Formation from Acetal ....	437
Formation from Sulphovinic acid ....	438
Preparation ....	439
Decompositions by $\text{HCl}$ , by $\text{PCl}^5$ , by $\text{PBr}^5$ , by $\text{C}^4\text{H}^6\text{O}^2$ and $\text{HCl}$ , and by $\text{COCl}$ ....	439, 440
Aldehyde with Acetic Anhydride, $\text{C}^4\text{H}^4\text{O}^2, \text{C}^8\text{H}^6\text{O}^8$ ....	440
Aldehyde with Chloride of Acetyl, $\text{C}^4\text{H}^4\text{O}^2, \text{C}^4\text{H}^3\text{O}^2\text{Cl}$ ....	441
Elaldehyde ....	441
Acetic acid: occurrence, natural formation and artificial synthesis ....	442
Acetates ....	442

# CONTENTS.

XXV

	Page
Acetonitrate of Baryta, $C^4H^3BaO^4, NO^6Ba + 8Aq$ ....	443
Acetonitrate of Strontia, $C^4H^3SrO^4, NO^6Sr + 3Aq$ ....	443
Acetate of Alumina ....	443
Double Acetates of Uranium, $MO, 2U^2O^3, 3C^4H^3O^3$ or $C^4H^3MO^4, 2C^4H^3(U^2O^3)O^4$ ....	443
Basic Acetate of Lead ....	445
Ferric Acetate ....	446
Peroxide of Acetyl, $C^4H^3O^2, O^2$ ....	446
Thiacetic acid, $C^4H^3O^2, H, S^2$ ....	446
Sulphide of Ethyl, $C^4H^6S$ ....	450
Iodide of Ethyl: preparation and action on silver-salts. — Bromide of Ethyl: preparation ....	451
Bromide of Ethylidine, $C^4H^4, Br^2$ ....	451
Chloride of Ethylidine, $C^4H^4, Cl^2$ ....	452
Oxychloride of Ethylidine, $C^8H^5Cl^2O^3$ ....	453
Chlorethylate of Ethylidine, $C^4H^4, C^4H^5O^2, Cl$ ....	454
Chlorosulphate of Ethyl, $C^4H^5ClS^2O^6$ ....	455
Ethylphosphoric acid, $PO^3, H^2, C^4H^3$ ....	456
Nitrate of Ethyl ....	456
Cyanide of Ethyl with Metallic Chlorides ....	457
Cyanide of Ethyl and Silver ....	458
Platinocyanide of Ethyl, $PtCy, C^4H^5Cy$ ....	459
Sulphocyanide of Ethyl ....	461
Sulphocyanide of Ethylene, $C^4H^4(C^2NS^2)^2$ ....	461

## ADDITIONS TO VOL. IX.

Acetone, $C^6H^6O^2$ ....	462
Monochloracetone, $C^6H^5ClO$ ....	463
Monobromacetone, $C^6H^5BrO^2$ . — Bichloracetone, $C^6H^4Cl^2O^2$ ....	464
Terchloracetone, $C^6H^3Cl^3O^2$ ; Tetrachloracetone, $C^6H^2Cl^4O^2$ ....	465
Pentachloracetone, $C^6HCl^5O^2$ ....	465
Hexachloracetone, $C^6Cl^6O^2$ ....	467
Action of Nitric Acid upon Acetone ....	468
Action of $PCl^5$ on Acetone: <i>Methylchloracetol</i> , $C^6H^6Cl^2$ ....	468
Acetone with Bisulphite of Ammonia, $C^6H^6O^2 + NH^4, H, 2SO^3$ ....	469
Action of Sodium on Acetone: <i>Pinacone</i> , $C^{12}H^{12}O^2$ ....	469
Action of Quick Lime on Acetone: <i>Oxide of Mesityl</i> , $C^{12}H^{10}O^2$ , and <i>Phorone</i> , $C^{18}H^{14}O^2$ ....	471
Methyl-acetone, $C^6H^5(C^2H^3)O^2$ ; Ethylacetone, $C^6H^5(C^4H^5)O^2$ and Dumasine, $C^{12}H^{10}O^2$ ....	473
Acetonic Acid, $C^8H^8O^6$ ....	475
Acetal, $C^{12}H^{14}O^4$ ....	476
Chloroacetals	
Monochloroacetal, $C^{12}H^{12}ClO^4$ ....	477
Bichloroacetal, $C^{12}H^{12}Cl^2O^4$ . — Terchloroacetal, $C^{12}H^{11}Cl^3O^4$ ....	478
Ethylamine: Formation ....	479



	Page
Separation of Ethylamine from Ammonia.—Sulphate of Ethylamine.— Phosphate of Ethylamine and Magnesia, $\text{PO}^3, \text{Mg}^2, \text{C}^4\text{H}^8\text{N}$	480
Ethylamine-alum, $4\text{SO}^4, \text{Al}^2, \text{C}^4\text{H}^8\text{N} + 24\text{Aq.}$ — Molybdate of Ethylamine, $\text{C}^4\text{H}^8\text{NO}, 2\text{MoO}^3$ . — Phosphomolybdate ....	481
Tetrethylum, $(\text{C}^4\text{H}^5)^4\text{N}$ .	
Iodide of Mercurotetrethylum, $\text{C}^{16}\text{H}^{19}\text{HgN}, \text{I}$ ....	482
Iodides of Tetrethylum and Mercury $(\text{C}^4\text{H}^5)^4\text{NI}, 2\text{HgI}$ and $(\text{C}^4\text{H}^5)^4\text{NI}, 3\text{HgI}$ ....	488
Trimethylethylum: <i>Teriodide</i> , $(\text{C}^2\text{H}^3)^3(\text{C}^4\text{H}^5)\text{N}, \text{I}^3$ and <i>Pentaiodide</i> , $(\text{C}^2\text{H}^3)^3(\text{C}^4\text{H}^5)\text{N}, \text{I}^5$ ....	484
Triethylmethylum: <i>Teriodide</i> , $(\text{C}^2\text{H}^3)(\text{C}^4\text{H}^5)^3\text{N}, \text{I}^3$ ....	485
Trimethylamylium: <i>Teriodide</i> , $(\text{C}^2\text{H}^3)^3(\text{C}^{10}\text{H}^{11})\text{N}, \text{I}^3$ ....	485
Ethylene-bases, $(\text{C}^4\text{H}^4)^n, \text{H}^4, \text{N}^2$ , &c. ....	486
Tetravinylium, $(\text{C}^4\text{H}^3)^4\text{N}$ ....	488
Sodium-ethyl, $\text{C}^4\text{H}^5\text{Na}$ ....	491
Compounds of Alcohol-radicals with Earth-metals ....	492
Ethyl- and Methyl-bases containing Arsenic and Phosphorus ....	492
Cacodyl-compounds:	
Terchloride, $\text{As}(\text{C}^2\text{H}^3)^2\text{Cl}^3$ ....	494
Chlorobibromide, $\text{As}(\text{C}^2\text{H}^3)^2\text{ClBr}^2$ . — Oxide, $\text{As}(\text{C}^2\text{H}^3)^2\text{O}$ ....	495
Arsenmethyl, $\text{AsC}^2\text{H}^3$ ....	495
Binoxide, $\text{AsC}^2\text{H}^3\text{O}^2$ ....	495
Arsenmethylic Acid, $\text{AsC}^2\text{H}^3, \text{H}^2, \text{O}^6$ ....	496
Bisulphide, $\text{AsC}^2\text{H}^3\text{S}^2$ ....	497
Biniodide, $\text{AsC}^2\text{H}^3\text{I}^2$ . — Bichloride, $\text{AsC}^2\text{H}^3\text{Cl}^2$ ....	498
Tetrachloride, $\text{AsC}^2\text{H}^3\text{Cl}^4$ ....	499
Stibethyl-compounds ....	499
Stibmethylethylum, $\text{Sb}(\text{C}^2\text{H}^3)(\text{C}^4\text{H}^5)^3$ ....	500
Zinc-ethyl: its action on Ammonia-bases ....	503
Zincamide, $\text{NH}^2\text{Zn}$ ....	503
Biethyl-zincamide, $\text{N}(\text{C}^4\text{H}^5)^2\text{Zn}$ . — Zincphenylimide, $\text{N}(\text{C}^{12}\text{H}^5)\text{HZn}$ . — Zinc-acetamide, $\text{N}(\text{C}^4\text{H}^3\text{O}^3)\text{HZn}$ . — Zinc-oximide $\text{N}(\text{C}^2\text{O}^4)^2\text{H}^2\text{Zn}^2$ ....	504
Stannethyls ....	505
Stannic Biethyl, $\text{Sn}(\text{C}^4\text{H}^5)^2$ ....	506
Bistannic Triethyl, $\text{Sn}^2(\text{C}^4\text{H}^5)^3$ ....	507
Stannic Ethylomethyl $\text{Sn}(\text{C}^2\text{H}^3)(\text{C}^4\text{H}^5)$ ....	509
Plumbethyls ....	510
Compounds of Biplumbic Triethyl, $\text{Pb}^2(\text{C}^4\text{H}^5)^3$ ....	511
Mercuric Ethyl, $\text{HgC}^4\text{H}^5$ ....	512
Oxalic Acid ....	514
Oxalates ....	515
Acid Oxalate of Soda, p. 515. — Oxalate of Lithia, 515. — Oxa- lates of Baryta and Strontia, 516. — Oxalate of Lime, 517. — Oxalate of Magnesia, 518. — Oxalate of Glucina and Ammonia, Oxalate of Manganese, 520. — Oxalate of Arsenious Acid and Potash, 521. — Oxalate of Antimony, 523. — Oxalate of Bis- muth, 524. — Oxalate of Cadmium, 525. — Stannous Oxalate, 526. — Ferrous Oxalate, 526. — Mercurous and Mercuric Oxalates, 527. — Oxalate of Silver, 528. — Sodio-platinous Oxalate, 529.	

	Page
Iodacetic Acid, $C^4H^3IO^4$ ....	529
Bibromacetic Acid, $C^4H^2Br^2O^4$ ....	531
Bromide of Bromethylene, $C^4H^3Br, Br^3$ ....	532
Chloracetene, $C^4H^3Cl$ ....	533
Chloral ....	533
Chloralide, $C^{10}H^2Cl^6O^6$ ....	534
Action of Chlorine on Acetic Ether ....	534
Acetamide. — Hydrochlorate of Acediamine ....	535
Oxamic acid ....	535
Oxamide ....	536
Urethane ....	537
Biethyl-urea ....	537
Allyl-compounds	
Allyl, $(C^6H^5)^2$ ....	538
Oxide; $(C^6H^5)^2O^2$ . — Ethyl-allyl-ether, $C^4H^5, C^6H^5, O^2$ ....	539
Allyl-alcohol, $C^6H^5, H, O^2$ . — Sulphide of Allyl, $(C^6H^5)^2S^2$ ....	540
Allyl-mercaptan, $C^6H^5, H, S^2$ . — Iodide of Allyl, $C^6H^5I$ . — Biniodide, $C^6H^5I^2$ ....	541
Bibromide, $C^6H^5Br^2$ . — Terbromide, $C^6H^5Br^3$ ....	542
Carbonate, $CO^2, C^6H^5$ . — Allyl-sulphuric acid, $C^6H^5, H, S^2O^8$ ....	543
Allylxanthic acid. — Cyanate of Allyl, $C^2NO^2, C^6H^5$ . — Sulpho- cyanide, $C^2NS^2, C^6H^5$ . — Acetate, $C^4H^3(C^6H^5)O^4$ ....	544
Butyrate, $C^8H^7(C^6H^5)O^4$ . — Valerate, $C^{10}H^9(C^6H^5)O^4$ . — Benzoate, $C^{14}H^5(C^6H^5)O^4$ . — Oxalate, $C^4(C^6H^5)^2O^8$ ....	545
Oxamate of Allyl, $C^4NH^3(C^6H^5)O^6$ . — Allyl-urea, $N^2.H^3, C^6H^5, C^2O^2$ . — Ethyl-allyl-urea, $N^2.H^3, C^4H^5, C^6H^5, C^2O^2$ . — Biallyl-urea, $N^2.H^2(C^6H^5)^2, C^2O^2$ ....	546
Allylamines ....	547
Tetrallylarsonium, $As(C^6H^5)^4$ . — Mercurallyl, $C^6H^5Hg^2$ ....	548
Bibromallylamine, $N, H(C^6H^4Br)^2$ ....	549
Ethylbibromallylamine, $N, C^4H^5(C^6H^4Br)^2$ ....	550
Acrolein ....	551
Bromide of Propylene ....	552
Bromide of Bromopropylene ....	552
Propylic Glycol, $C^6H^8O^4$ ....	554
Butylic Glycol, $C^8H^{10}O^4$ ....	556
Amylic Glycol, $C^{10}H^{12}O^4$ ....	557
Propionic acid ....	558
Chloropropionic acid ....	559
Butyracetic acid ....	560
Malonic acid, $C^6H^4O^6$ ....	560
Cyanurate of Ethyl, $C^{18}H^{15}N^3O^6 = Cy^3(C^4H^5)^3O^6$ ....	562
Chlorocyanuric Ether, $C^{18}H^{11}Cl^4N^3O^6$ ....	563
Hydrochlorate of Cyanic Ether, $C^6H^5NO^2, HCl$ ....	563
Biethylcyanuric acid, $C^{14}H^{11}N^3O^6 = Cy^3(C^4H^5)^2HO^6$ ....	565
Liquid Chloride of Cyanogen, $Cy^2Cl^2$ ....	565
Cyanetholine, $C^6H^5NO^4$ ....	566

	Page
Glycerin : its formation ....	566
Conversion of Glycerin into Sugar ....	567
Solubility of Lime in Aqueous Glycerin ....	568
Glyceric acid, $C^6H^6O^3$	
Glycerides :	
Bromhydrins ....	572
Monobromhydrin, $C^6H^7BrO^4$ . — Bibromhydrin, $C^6H^6Br^2O^3$ ....	574
Terbromhydrin, $C^6H^5Br^3$ . — Epibromhydrin, $C^6H^5BrO^3$ ....	575
Hexaglyceric Bromhydrin, $C^{26}H^{27}BrO^4$ . — Hemibromhydrin, $C^{12}H^9BrO^4$ ....	576
Biepipibromhydrophosphoryl, $C^{12}H^9Br^3P$ ....	577
Chlorhydrins :	
Terchlorhydrin, $C^6H^5Cl^3$ . — Epibichlorhydrin, $C^6H^4Cl^2$ ....	577
Bibromochlorhydrin, $C^6H^5Br^2Cl$ . — Bromobichlorhydrin, $C^6H^5BrCl^2$ ....	578
Acetochlorhydrins :	
Acetochlorhydrin, $C^{10}H^9ClO^6$ . — Acetobichlorhydrin, $C^{10}H^8Cl^2O^4$ ....	579
Biacetochlorhydrin, $C^{14}H^{11}ClO^8$ . — Acetochlorobromhydrin, $C^{10}H^8BrClO^4$ ....	580
Glycerides of Polybasic acid ....	580
Nitroglycerin ....	583

### ADDITIONS TO VOL. XIII.

Anisates ....	584
Nitranisates ....	585
Caprylic Alcohol. — Chloride of Capryl. — Acetate of Capryl ....	587
Chloride of Caprylene ....	588

### ERRATA.

Page.	Line.				
10	16 from top	for	$C^{16}H^{16}O^3$	read	$C^{16}H^6O^3$
12	16	„	$C^{16}H^6MO^8$	„	$C^{16}H^5MO^8$
„	17	„	$C^6H^5M^2O^8$	„	$C^{16}H^4M^2O^8$
15	18	„	$C^{14}$	„	$C^{16}$
74	11 from bottom	„	Argentammonium	„	Silver and Ammonium
126	20 from top	„	$C^{16}H^6NH^4O^4$	„	$C^{16}H^7(NH^4)O^6$
129	8 and 10	„	$H^9$	„	$H^7$
143	7 from bottom	„	$C^{26}$	„	$C^{16}$
172	17 from top	„	$C^{24}NH^{28}$	„	$C^{24}NH^{28}$
189	6	„	$NaO^2SO^2$	„	$NaO, 2SO^2$
239	20	„	dele “ and calcium ”		

## COMPOUNDS CONTAINING 16 AT. CARBON.

### *Primary Nucleus C<sup>16</sup>H<sup>8</sup>.*

#### **Styrol. C<sup>16</sup>H<sup>8</sup>.**

- BONASTRE. (1831.) *J. Pharm.* 17, 338; *N. Tr.* 24, 2, 236; *Pharm. Centr.* 1831, 412.  
F. D'ARCET. *Ann. Chim. Phys.* 66, 110; *J. pr. Chem.* 13, 428.  
MULDER. *J. pr. Chem.* 15, 307.  
E. SIMON. *Ann. Pharm.* 31, 265; *Pharm. Centr.* 1839, 358.  
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GERHARDT & CAHOUS. *N. Ann. Chim. Phys.* 1, 96; *Ann. Pharm.* 35, 67; *J. pr. Chem.* 23, 321.  
E. KOPP. *Compt. Rend.* 21, 1378; *J. pr. Chem.* 37, 281; *Pharm. Centr.* 1846, 237; *Compt. chim.* 1846, 87; 1850, 141; *Ann. Pharm.* 60, 269.  
BLYTH & HOFMANN. *Ann. Pharm.* 53, 292, 325; *Pharm. Centr.* 1845, 403.  
HEMPEL. *Ann. Pharm.* 59, 316; *Pharm. Centr.* 1847, 101.  
SCHARLING. *Ann. Pharm.* 97, 184.

#### *Volatile Oil of Liquid Storax, Cinnamene, Cinnamomin, Cinnamol; Cinnamène.*

Cinnamene, which was first obtained by Simon and Herzog, mixed with a large quantity of benzin, then pure by Gerhardt and Cahours, was considered by them, as well as by E. Kopp, to be identical with the oil of *Storax liquidus* first obtained by Bonastre, and more thoroughly investigated by Simon, although the former is not converted into solid metastyrol by heating. Blyth and Hofmann conjecture that the cinnamene is mixed with other hydrocarbons, resulting from the distillation of the cinuamate of baryta, which prevent the transition to the solid state; this is rendered more probable by Hempel's experiments, who seems to have obtained real styrol by distilling cinnamate of copper, and by passing cinnamic acid vapour through a red-hot tube. It appears doubtful, whether the cinnamol which Scharling obtained by distilling the resin of Peruvian balsam, is identical with styrol, on account of the difference in its boiling point, and its behaviour with oxygen.

*Source.* In *Storax liquidus*.

*Formation.* 1. Hempel obtained styrol by the action of a red heat upon cinnamic acid.— 2. Cinnamene is formed in the dry distillation of cinnamic acid with excess of caustic baryta (Gerhardt & Cahours); or with potash, in which case a considerable quantity of benzol is formed (Simon, Herzog, Blyth & Hofmann); in the dry distillation of cinnamate of copper. (E. Kopp, Hempel.)— 3. The oil which Mulder obtained by the action of a red heat on oil of cinnamon, and the oil obtained by F. d'Arcet, in the same way from camphor, have properties similar to those of cinnamene.— 4. The oil arising from the dry distillation of dragon's blood contains styrol, which is converted into metastyrol by rectification.— 5. The oil named by Couerbe, *Octocarbure quadrihydrique*, which passes over after the toluol in the rectification of resin-oil, seems to be a kind of styrol.— 6. In the dry distillation of the resin of Peruvian balsam mixed with pumice stone, a distillate is obtained, containing benzoic acid, wood spirit, and cinnamol. (Scharling.)

1. *Preparation of Styrol.* 10 lbs. of liquid storax are distilled with 7 lbs. of crystallised carbonate of soda (in order to retain cinnamic acid), and 60 to 70 quarts of water. An aqueous milky distillate, with a light yellow oil swimming upon it, then passes over, which is freed from water by chloride of calcium. (Simon, Blyth & Hofmann.) Out of 41 lbs. of liquid storax, 12oz. of styrol were obtained by distillation; another time, only 3oz. were obtained out of 24 lbs. of older storax. (Blyth & Hofmann.)— Simon took for 20 lbs. of storax, 14 lbs. of crystallised carbonate of soda; Blyth and Hofmann found that 7 lbs. were sufficient.— The quantity of styrol obtained from 20 lbs. of liquid storax, varies from 1oz. to 5½oz., probably in consequence of the storax being prepared by melting out, in which operation, varying quantities of oil are lost, and because the older the storax, the smaller is the proportion of styrol contained in it. (Simon.) E. Kopp distils liquid storax with 5 or 6 times its weight of pure water, because soda causes considerable frothing and overflowing. In order to obtain styrol perfectly colourless, it is rectified, about one-third being thereby converted into metastyrol, which remains behind. (Blyth & Hofmann.) Resin of Peruvian balsam, mixed with fragments of pumice, is heated in a retort to dull redness; and the oil which passes over, together with benzoic acid and an aqueous liquid, is subjected to fractional distillation. The part which passes over under  $175^{\circ}$ , and is lighter than water, is collected, repeatedly distilled with solution of caustic potash, allowed to stand several days over pieces of caustic potash, and then distilled at a temperature not exceeding  $150^{\circ}$ . The distillate is dried with chloride of calcium, treated with potassium, whereby hydrogen is evolved, and the fluid part is decanted from the resulting gelatinous precipitate, and distilled; the boiling point gradually rises from  $100^{\circ}$  to  $140^{\circ}$ , at which point all the styrol has passed over, whilst metastyrol remains behind, to the amount of two-thirds of the liquid employed. (Scharling.)

2. *Preparation of Cinnamene.* 1 part of cinnamic acid is distilled at a gentle heat with 4 parts of caustic baryta. With careful heating the residue is but little blackened, and nothing is formed but carbonic acid and cinnamene.— When 1 part of cinnamic acid is distilled over a naked

charcoal fire with 3 pts. of dry caustic potash, the heat being gradually raised, first water passes over, and then a clear oil, which at last is tinged brown, whilst carbonate of potash and charcoal remain in the retort. The oil which has passed over is rectified. (Simon, Herzog.)—Mitscherlich (*Lehrb.* 4 ed., 1,179) showed that the oil thus obtained, which according to Herzog, boiled at  $89^{\circ}$ , could not be a pure product; Blyth and Hofmann found, that by submitting it to fractional distillation, benzol distilled over at  $100^{\circ}$ ; that which passed over afterwards could not be obtained at constant boiling point, the thermometer gradually rising to  $200^{\circ}$ . The distillate at  $140^{\circ}$  formed with bromine a white crystalline mass, similar in its properties to bromide of styrol.

3. If the vapour of cinnamic acid be passed through a tube filled with fragments of glass, at a dull red-heat, a dark brown liquid is obtained, which on rectifying with water, yields pure styrol. (Hempel.)—4. Cinnamate of copper (obtained by precipitating the potash salt with sulphate of copper, washing the precipitate and drying at  $100^{\circ}$ ) is submitted to distillation, and the colourless oil which has passed over, is freed from undecomposed cinnamic acid with dilute potash, washed with water, dried with chloride of calcium, and rectified. (Hempel, E. Kopp.)—5. Vapour of oil of cinnamon, or oil of cassia, is passed through a tube heated to bright redness, the receiver being cooled with a freezing mixture. (Mulder.)—6. Vapour of camphor is passed over iron at a red heat, and the resulting oil is rectified at  $145^{\circ}$ . (F. d'Arcet.)—7. On rectifying the oil obtained by the dry distillation of dragon's blood, an oil is obtained at  $180^{\circ}$ , which by repeated distillation, at first yields only toluol, then a mixture of toluol and styrol, and lastly pure styrol. (Blyth & Hofmann.)

*Properties.* Styrol is mobile and perfectly limpid (Simon, Blyth & Hofmann); refracts light like creosote. (Simon.) Index of refraction for the red ray = 1.532 (Blyth & Hofmann), 1.505. (Scharling.) Like liquid storax, it has an odour of naphthalin (Simon); it has a strongly persistent peculiar aromatic odour of benzol and naphthalin, and a burning taste. (Blyth & Hofmann.) Sp. gr. = 0.924. Boils at  $145.75^{\circ}$ . Makes grease-spots on paper which rapidly disappear. (Blyth & Hofmann.) Boils below  $140^{\circ}$ . (Scharling.) Becomes somewhat less mobile at  $-20^{\circ}$ , but does not solidify. It is converted into solid metastyrol when heated, either to its boiling point, or for half an hour to  $200^{\circ}$ , or when kept at  $100^{\circ}$  for a considerable time in a sealed glass tube. (See *Metastyrol*.) (Blyth & Hofmann, Hempel.)—*Cinnamene* is perfectly limpid and smells very much like benzol (Gerhardt & Cahours); has an odour very like that of styrol, but more pleasant (Blyth & Hofmann); it is colourless, very mobile, refracts light very strongly like bisulphide of carbon; has a penetrating aromatic odour, and a burning, peppery, aromatic taste, leaving a sweetish after-taste. (E. Kopp.) Sp. gr. 2.951 at  $0^{\circ}$  [it should be 0.951. *Gm.*] at  $15^{\circ}$  only = 0.928. (E. Kopp.) Vapour density = 3.55. (Cahours & Gerhardt.) Boils at  $140^{\circ}$  (Cahours & Gerhardt); at  $144^{\circ}$ . (E. Kopp.) When pure cinnamene is reduced to one-fifth of its bulk by distillation, the residue is pale yellow and very thick, but never so solid as in the case of styrol; the residue on being entirely distilled, yields perfectly fluid cinnamene. (E. Kopp.) The oil which Hempel obtained, by distilling cinnamate of copper, or by passing the vapour of cinnamic acid through a red-hot tube, yielded metastyrol when rectified.

The oil obtained by passing the vapour of camphor over red-hot iron,

is of a pale yellow colour, lighter than water, and has a peculiar odour which is different from that of camphor, if the distillation be conducted slowly. (F. d'Arcet.) The oil obtained by passing the vapour of oil of cinnamon or of cassia through a red-hot tube, remains fluid at  $10^\circ$ , and boils at  $153^\circ$ . (Mulder.) Couerbe's *Octocarbure quadrihydrique*, is a pale yellow liquid, of sp. gr. 0.838; it smells strongly of phosphoretted hydrogen, and distils between  $135^\circ$  and  $140^\circ$ .— Vapour density = 3.765. It rapidly absorbs oxygen from the air, and reddens on the addition of sulphuric acid.

				Blythe & Hofmann.		Hempel.		F. d'Arcet.		Mulder.		
16 C	....	96	....	92·31	.....	92·37	....	91·09	....	91·08	....	90·79
8 H	....	8	....	7·69	.....	7·92	....	8·05	....	7·65	....	7·88
<hr/>												
C <sup>16</sup> H <sup>8</sup>	....	104	....	100·00	.....	100·29	....	99·14	....	98·73	....	98·67

					Gerhardt & Cahours.		Couerbe.		Scharling.
16 C	.....				92.35	.....	91.80	.....	91.93
8 H	.....				7.70	.....	7.77	.....	8.07
$C^{16}H^8$	.....				100.05	.....	99.57	.....	100.00

			Vol.		Density.
C. Vapour	.....	16	.....		6.6560
H-Gas	.....	8	.....		0.6544
Styrol vapour	.....	2	.....		7.3104
		1	.....		3.6552

*Decompositions.* 1. The vapour of styrol may be passed through a red-hot glass tube without decomposing. A cotton wick steeped in styrol, burns with a bright and very smoky flame. (Blyth & Hofmann.) It absorbs free oxygen at common temperatures. (Bonastre, Blyth & Hofmann.) Styrol absorbs oxygen slowly (17.2 per cent. in five months), and forms a soft amorphous mass, which yields but little pure acid when treated with ammonia; the soda-salt of this acid in alcoholic solution, gives an abundant precipitate with nitrate of silver, which soon blackens, and corresponds to the formula  $C^{12}H^5AgO^4$ ; the portion insoluble in ammonia contains metastyrol and a soft resin of an agreeable odour, soluble in ether. The styrol obtained from the resin of Peruvian balsam, absorbs less oxygen (scarcely 4 per cent.), and becomes gradually filled with long crystalline needles, which dissolve with the gentlest heat, and form with ammonia, a yellow oily liquid, which is readily soluble in alcohol, and on evaporating, yields a crystalline salt mixed with resin, which on being recrystallised from water, gives a small precipitate with nitrate of silver, moderately soluble in water. This precipitate blackens in the dark, and contains 53.8 per cent.  $AgO$ , so that it cannot contain benzoic acid; no metastyrol is formed. (Scharling.) — 2. Styrol is resinised by distillation with nitric acid, benzoic and hydrocyanic acids being formed, as well as nitrostyrol and a resin. (Simon.) Common nitric acid acts very slowly on styrol when merely warmed with it; on boiling, the styrol becomes yellow, and distils over with the acid but slightly altered, and only after being redistilled five or six times, becomes more viscid, at last sinks to the bottom, and solidifies into a



brown resin on cooling. The oily drops which pass over with the water, no longer smell of styrol, but peculiarly sharp, like cinnamon, and excite tears; they are a solution of nitrostyrol in other oils, probably styrol and oil of bitter almonds, and solidify at  $20^{\circ}$  into a crystalline mass, which leaves crystals of nitrostyrol on being pressed. The aqueous acid liquid deposits on cooling, crystals of benzoic and nitrobenzoic acids; the resinous residue, after being repeatedly washed with water, dissolves for the most part in boiling water, whilst nitrostyrol evaporates with the steam; when no more nitrostyrol passes over, the solution solidifies on cooling into a crystalline mass, consisting of benzoic and nitrobenzoic acids, the relative quantities of which depend upon the strength of the nitric acid; undiluted commercial nitric acid yields principally nitrobenzoic acid, while the diluted acid yields chiefly benzoic acid, which on boiling, partly evaporates with the nitrostyrol. The formation of benzoic acid is probably preceded by that of oil of bitter almonds, at least the distillate at a certain period smells decidedly of that substance; prussic acid does not appear to be present. Styrol dissolves in fuming nitric acid with great evolution of heat, and forms a deep red solution; red vapours are, however, evolved, even when the styrol is gradually added and the liquid artificially cooled. Water precipitates from the solution a soft yellow resin, of the odour of nitrostyrol, which, after washing with water, yields by distillation with water, rather more nitrostyrol than is obtained by the use of a weaker acid. (Blyth & Hofmann.)

Cinnamene is converted by nitric acid into a crystalline mass, which appears to be benzoic acid. (Gerhardt & Cahours.) When gradually dropped into fuming nitric acid, it dissolves with considerable evolution of heat and red vapours; water precipitates from the solution a resin, which yields nitrostyrol when distilled with water. On boiling with an excess of concentrated nitric acid, the solution becomes filled, when cool, with needles of nitrobenzoic acid. (E. Kopp.) — 3. When nitrous acid is passed through heated styrol, a violent reaction takes place and vapours are evolved which possess the irritating odour of nitrostyrol, and an inodorous crystalline substance is formed, almost insoluble in water, alcohol and ether; this substance has not been more closely investigated. (Blyth & Hofmann.) — 4. When styrol is distilled with sulphuric acid, bichromate of potash and water, much unaltered styrol passes over with the vapour of water: it is only when the residue becomes thicker that an action takes place; and on continuing the distillation, crystals of benzoic acid begin to float on the distillate. (Blyth & Hofmann.) Cinnamene mixed with concentrated chromic acid, solidifies almost immediately into a blackish brown mass.—On boiling this mass with water, the chromic acid is reduced and white sublimed crystals of benzoic acid are formed. (E. Kopp.)

5. Styrol absorbs *chlorine* with avidity. If the gas is slowly passed through, and the styrol kept cool and protected from sunlight, no hydrochloric acid is evolved and the oil is completely converted into thick *chloride of styrol*; if more chlorine is passed through the liquid, an evolution of hydrochloric acid commences, because the hydrogen in the styrol then begins to be replaced by chlorine. When chlorine is passed through styrol exposed to sunshine, a large quantity of hydrochloric acid is evolved, and the oil, after several days, becomes converted into a viscid liquid which evolves still more hydrochloric acid if the action of chlorine be continued. (Blyth & Hofmann.) — 6. With excess of *bromine*, styrol becomes heated almost to boiling, evolves hydrobromic acid, and is con-



verted into solid *bromide of styrol*. If bromine be very slowly added to styrol, the whole being kept cool, no hydrobromic acid is evolved. (Blyth & Hofmann.) Cinnamene forms, with excess of bromine, a solid crystalline mass of bromide of styrol. On adding the bromine gradually, no hydrobromic acid is evolved. (Gerhardt & Cahours, E. Kopp, Blyth, and Hofmann.)—7. With hydrochloric acid and chlorate of potash styrol behaves in the same manner as with chlorine. (Blyth & Hofmann.) With fuming sulphuric acid styrol becomes viscid and dark-coloured; water precipitates a brownish resin from the solution, and the acid filtrate forms, with carbonate of baryta, a soluble salt, which cannot be obtained crystallized, and probably contains an acid analogous to benzosulphuric acid. (Blyth & Hofmann.) Fuming sulphuric acid seems to form a conjugated acid with cinnamene. (Gerhardt & Cahours.)

*Combinations.* Styrol is very slightly soluble in water, but imparts to it its smell and taste; the undissolved styrol at the same time takes up a very small quantity of water. (Blyth & Hofmann.)—Cinnamene is not soluble in water.

Styrol, heated with phosphorus or sulphur, dissolves a considerable quantity, which crystallises out on cooling. It dissolves in bisulphide of carbon. (Blyth & Hofmann.)—Cinnamene is soluble in bisulphide of carbon.

Styrol is miscible in all proportions with absolute alcohol, and dissolves less in aqueous alcohol the more water the latter contains; it mixes with ether in all proportions, and is soluble in wood-spirit, acetone, and in oils, both fat and volatile. (Blyth & Hofmann.)—Cinnamene dissolves in alcohol, ether, and in volatile oils.

Caoutchouc swells up in heated styrol, but dissolves only to a slight extent. (Blyth & Hofmann.)

### Metastyrol. $C^{10}H^8$ .

GLENARD & BOUDAULT (1844). *Compt. rend.* 19, 509; *N. J. Pharm.* 6, 257; *J. pr. Chem.* 33, 466.

E. SIMON. *Ann. Pharm.* 31, 266; *Pharm. Centr.* 1839, 858.

BLYTH & HOFMANN. *Ann. Pharm.* 53, 311; *Pharm. Centr.* 1845, 423.

HEMPEL. *Ann. Pharm.* 59, 316; *Pharm. Centr.* 1847, 101.

#### *Draconyl, Oxide of Styrol.*

*Formation and Preparation.* 1. When the oil obtained by the dry distillation of dragon's blood is distilled with water in order to purify it, and then rectified, there remains in the retort a mixture of metastyrol with a certain quantity of toluol, from which the toluol is removed by alcohol, the metastyrol being left behind as a colourless, soft, resinous mass. After being repeatedly washed with alcohol and dried with frequent stirring at  $150^{\circ}$ , it becomes perfectly solid. (Glenard & Boudault.)

2. When anhydrous styrol is heated in a retort fitted with a thermometer, copious vapours are evolved between from  $100^{\circ}$  to  $120^{\circ}$ ; at  $145^{\circ}$ , the mass begins to boil and a considerable quantity of styrol passes

over, the thermometer remaining stationary; but it suddenly begins to rise, and so rapidly that it must be quickly removed from the retort. The liquid has then become thickish, and scarcely anything more distils over; on cooling, the mass solidifies into a transparent glass, which is metastyrol, amounting to more than one-third of the styrol employed. Simon regarded it as resinized styrol, and called it *Oxide of Styrol*.—Styrol inclosed in sealed glass bulbs, placed in boiling water, becomes thick in two days, and is completely solid on the third; in a strong glass tube, at 200°, the change takes place in half an hour. — Styrol exposed in glass bulbs to the hot summer's sun, requires three weeks for its conversion; perhaps the light also acts in this case, since styrol, preserved in the dark, remained fluid for five years. — In order to purify metastyrol from styrol for analysis, it is boiled with ether till it swells into a jelly; the ether which has dissolved the accompanying styrol is poured off, and the residue dried in a water-bath. All the ether then evaporates and the metastyrol remains as a white, inodorous, tasteless, and easily friable sponge; it is finely pulverised, boiled with alcohol, and dried.

3. On rectifying the oil obtained by the dry distillation of cinna-mate of copper, a certain quantity of metastyrol remains in the retort. (Hempel.)

*Properties.* Metastyrol is perfectly limpid, and refracts light as strongly as styrol. (According to Scharling, the index of refraction of thick, turpentine-like metastyrol, for the red ray, is only 1.459. *Ann. Pharm.* 97, 187.) At the ordinary temperature, it is solid, and may be cut with a knife; when heated, it becomes soft and thready, like melted glass, and is quite destitute of taste and odour. (Blyth & Hofmann.) Sp. gr. = 1.054 at 13°. (Scharling.) On continued heating it becomes again fluid, and distils, all but a trace, as pure styrol. (Blyth & Hofmann.) Glenard & Boudault, who had not remarked this property, assert that draconyl is not volatile of itself, but that it may be distilled together with another hydrocarbon.

					Glenard & Boudault.		Blyth & Hofmann.		Hempel.		Scharling.
16 C ...	96	...	92·31	.....	92·32	...	92·05	...	92·10	...	91·93
8 H ...	8	...	7·69	.....	7·81	...	8·00	...	7·98	...	8·07
<hr/>											
C <sup>14</sup> H <sup>8</sup> ...	104	...	100·00	.....	100·13	...	100·05	...	100·08	...	100·00

Metastyrol is isomeric or polymeric with styrol.

It burns with a smoky flame. (Glenard & Boudault.)

*Decompositions.* 1. Metastyrol is not attacked by common nitric acid, but is dissolved by fuming nitric acid, with evolution of red vapours; water precipitates nitrometastyrol from the solution. (Glenard & Boudault, Blyth & Hofmann.) If the boiling be continued too long, water likewise precipitates a substance richer in carbon and poorer in nitrogen. (Blyth & Hofmann.)—2. Strong sulphuric acid is without action in the cold, but on heating, sulphurous acid is evolved and the metastyrol becomes charred. (Glenard & Boudault, Blyth & Hofmann.)

*Combinations.* Metastyrol does not dissolve in water or alcohol, either hot or cold (Glenard & Boudault, Blyth & Hofmann.) In boiling

ether, it swells up to six or eight times its volume, whilst a small quantity dissolves and is deposited on evaporation as a thin transparent film. Oil of turpentine also dissolves traces of it. (Blyth & Hofmann.) It dissolves with the aid of heat in volatile and fatty oils, but separates out on cooling. (Blyth & Hofmann.)

### Toluylic Acid.



NOAD. (1847.) *Phil. Mag. J.* 32, 19; *Ann. Pharm.* 63, 288; *Mem. Chem. Soc.* 3, 425; *J. pr. Chem.* 44, 145; *Pharm. Centr.* 1848, 178. K. KRAUT. *Inaug. dissert. on Cuminol and Cymene.* Gött. 1854, p. 20.

*Formation.* By the action of dilute nitric acid on cymene.

*Preparation.* 1 pt. of cymene is distilled in a spacious retort with 4 pts. of a mixture of common nitric acid with 6 times its volume of water, the distillate being repeatedly poured back into the retort. The reaction takes place quietly, the oil first becoming blue, then dark yellow, then viscid, and finally sinking to the bottom. The operation is finished when the drops of oil which at first float upon the distillate are replaced by white crystals, and the retort on cooling becomes filled with white crystals. (Noad.) If this method is exactly followed, which requires continuous boiling for a week, and the toluylic acid, as it is formed, is removed so as to prevent any further action of the nitric acid, the acid obtained is perfectly pure. (Kraut.) — The toluylic acid is the purer the weaker the nitric acid, and the more slowly the distillation is conducted; stronger acid acts violently, and forms nitrotoluylic acid, which is difficult to separate. In order to effect the separation, the mixture is first freed from nitric acid and a yellow resin by boiling with milk of lime; the filtered solution of the lime-salt is then precipitated by hydrochloric or nitric acid; the precipitated acids are dissolved in baryta water, and evaporated on a water-bath; the residue is treated with water; the solution filtered from the nitrotoluylate of baryta, which is difficultly soluble, is next evaporated, again treated with cold water, and filtered; and this treatment is repeated till no more nitrotoluylate of baryta separates out. The liquid is then precipitated by an acid, and the product is recrystallised. (Noad.)

*Properties.* Toluylic acid is precipitated from its salts by nitric or hydrochloric acid, as a white curdy mass consisting of microscopic needles; it crystallises from hot water in needles. Melts when heated and sublimes without decomposition in beautiful needles. When perfectly pure it is inodorous and tasteless, but when slightly impure it has a peculiar repulsive odour, slightly resembling that of bitter almonds.

					Noad.		Kraut.
16 C	.....	96	...	70.58	.....	70.20	..... 70.18
8 H	.....	8	...	5.88	.....	5.97	..... 5.67
4 O	.....	32	...	23.54	.....	23.83	..... 24.15
$C^{16}H^8O^4$	.....	136	...	100.00	.....	100.00	..... 100.00

Isomeric with benzoate of methyl and hydride of anisyl.

*Decompositions.* Toluylic acid splits up into carbonic acid and toluo when heated with baryta or lime:



2. When boiled with strong nitric acid, it forms nitrotoluylic acid. (Noad.) In the animal organism, it is converted into a crystalline, indifferent body, which may be separated from the urine by ether. (Hofmann, *Ann. Pharm.* 74, 342.) After taking toluylic acid, ether separates from the urine a crystallisable substance which is precipitated in the amorphous state from its ammoniacal solution by acids, and forms a silver-salt which readily blackens. (Kraut.)

*Combinations.* Toluylic acid dissolves largely in boiling water, and crystallises out on cooling.

The salts of toluylic acid ( $C^{16}H^7MO^4$ ) are obtained by direct combination or by double decomposition.

*Toluylate of Ammonia* forms small prisms.

*Toluylate of Potash* is obtained by exactly neutralising the acid with potash; it forms long shining needles.

*Toluylate of Baryta*, prepared like the preceding, forms confused crystals.

					Noad.
$C^{16}H^7O^3$	.....	128.0	...	62.56	
BaO	.....	76.6	...	37.44	..... 37.37
<hr/>					
$C^{16}H^7BaO^4$	.....	204.6	...	100.00	

*Toluylate of Lime* crystallises from its concentrated aqueous solution in long shining needles.

*Toluylate of Copper.* — The potash-salt forms with sulphate of copper a bright blue precipitate, which is sparingly soluble in water, and dissolves with dark blue colour in ammonia.

					Noad.
$C^{16}H^7O^3$	.....	128.0	...	76.28	
CuO	.....	39.8	...	23.72	..... 24.28
<hr/>					
$C^{16}H^7CuO^4$	.....	167.8	...	100.00	

*Toluylate of Silver.* — On precipitating neutral toluylate of ammonia with nitrate of silver, a curdy precipitate is formed, which is washed with cold water. It crystallises from hot water in small needles.

					Noad.
16 C	.....	96	...	39.55	..... 39.20
7 H	.....	7	...	2.88	..... 3.03
Ag	.....	108	...	44.44	..... 44.44
4 O	.....	32	...	13.13	..... 13.33
<hr/>					
$C^{16}H^7AgO^4$	.....	243	...	100.00	..... 100.00

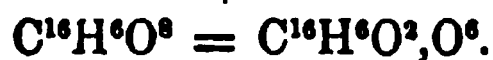
**Toluylate of Ethyl.**

NOAD. *Ann. Pharm.* 63, 295; *Pharm. Centr.* 1848, 170.

Hydrochloric acid gas is passed into a solution of toluylic acid in absolute alcohol until it is saturated; about two-thirds are then distilled off, and the residue is mixed with water, which separates out a heavy black oil. This is purified from free acid by digestion in ammonia, washed with water, dried with chloride of calcium, and rectified.

Colourless liquid, which boils at  $228^\circ$ , has a pleasant odour like cinnamic and benzoic ethers, and a sweetish taste,

					Noad.
20 C .....	120	...	73.17	.....	72.90
12 H .....	12	...	7.32	.....	7.52
4 O .....	32	...	19.51	.....	19.58
<hr/>					
$C^{20}H^{12}O^4$ .....	164	...	100.00	.....	100.00

**Oxygen-nucleus  $C^{16}H^{16}O^3$ .****Phthalic Acid.**

LAURENT. *Ann. Chim. Phys.* 61, 113; *J. pr. Chem.* 8, 13; *Ann. Pharm.* 19, 38; *Pharm. Centr.* 1836, 442; *Rev. scient.* 6, 76; 9, 31; *Ann. Pharm.* 41, 107.

MARIGNAC. *Bibl. univ.* 86, 370; *Ann. Pharm.* 42, 215; *Pharm. Centr.* 1842, 575.

SCHUNCK. *Ann. Pharm.* 66, 197; *Phil. Mag. J.* 32, 138; 35, 212; *Pharm. Centr.* 1848, 627.

WOLFF & STRECKER. *Ann. Pharm.* 75, 12, 25; *Pharm. Centr.* 1850, 596.

**Alizaric Acid — Naphthalic Acid.** — Obtained by Laurent, in 1836, by treating the bihydrochlorate of bichloronaphthalin with nitric acid; and recognized by Gerhardt (*Compt. Chim.* 1849, 222), and by Wolff & Strecker, as identical with Schunck's alizaric acid.

**Formation.** Phthalic acid is formed, together with oxalic acid, by continued heating of naphthalin with nitric acid;



2. Also by the action of nitric acid on bihydrochlorate of bichloronaphthalin ( $C^{20}H^8Cl^4$ ) or bihydrochlorate of tetrachloronaphthalin ( $C^{20}H^7Cl^6$ ).—

8. Likewise, by the oxidation of alizarin and purpurin with dilute nitric acid or a ferric salt. (Schunck, Wolff & Strecker.)



**Preparation.** 1. The liquid obtained by prolonged boiling of naphthalin with nitric acid is treated with water, after the nitro-compounds have separated from it, in order to precipitate the remainder of those compounds; and on evaporating the aqueous liquid to a syrup, treating the residue with water, filtering and again evaporating, crystals of nitrophthalic acid are obtained. The mother-liquor, neutralised with ammonia, solidifies into a crystalline mass, the hot aqueous solution of which deposits small uncrystallised plates of nitrophthalate of ammonia. The mother-liquor of this salt yields, by evaporation, brown grains of phthalate of ammonia, which are picked out, dissolved in boiling water and treated with a few drops of ammonia. The solution yields six-sided tablets of the salt. (Laurent.)—2. 1 pt. of bihydrochlorate of bichloronaphthalin is boiled in a retort with from 4 to 5 pts. of common nitric acid (if 15 to 20 grammes are employed, it is necessary to heat it for at least a whole day); the liquid is evaporated to dryness; the yellow crystalline residue treated with water; the whole boiled till the greater part is dissolved; and the solution filtered is boiled from the brown residue and allowed to cool. — The acid then crystallises out in reddish-yellow pearly plates, and the mother-liquor yields an additional quantity after evaporation; the acid is obtained colourless by recrystallisation or by subliming and dissolving the anhydride in boiling water. (Laurent, Marignac.)—The naphthalic acid described by Marignac (*Ann. Pharm.* 38, 14) appears to be phthalic acid containing nitrophthalic acid. — 3. Alizarin (*garancin*) is heated with nitric acid of sp. gr. 1.20 till no more nitrous fumes are evolved, the dark brown alizarin turning yellow. The reddish yellow solution, on being evaporated till it crystallises, yields a yellow mass of crystals consisting of oxalic and phthalic acids; this is washed with cold water and dissolved in boiling water; the solution is neutralised with lime; and the filtrate treated with hydrochloric acid and evaporated till it crystallises. The yellow residue, after being freed from chloride of calcium with cold water, is dissolved in hot water, and the solution is decolorised with animal charcoal, and evaporated till it crystallises. If the acid is not completely decolorised by the animal charcoal, chlorine must be passed through the boiling solution. (Schunck.) Wolff & Strecker obtained considerable quantities of the acid by heating impure alizarin and crude madder with nitric acid; see also Gerhardt. (*Compt. Chim.* 1849, 220.) — Purpurin is dissolved in excess of nitric acid, the solution evaporated, and the yellowish crystalline plates washed with cold water. (Wolff & Strecker.)

**Properties.** Phthalic acid forms white plates of a pearly lustre. (Marignac.) — Colourless, transparent, rhombic tablets. (Schunck.) Melts when heated, reddens litmus, and tastes acid. (Schunck.)

					Laurent.		Marignac,		Schunck.	
16 C	.....	96	...	57.84	.....	58.35	...	57.66	....	57.46
6 H	.....	6	...	3.61	.....	3.11	...	3.67	....	3.91
8 O	.....	64	...	38.55	.....	38.54	...	38.67	....	38.63
<hr/>										
C <sup>16</sup> H <sup>6</sup> O <sup>8</sup>	.....	166	...	100.00	.....	100.00	...	100.00	....	100.00

The acid analysed by Laurent and by Marignac, was prepared according to No. 2, that by Schunck, according to No. 3.

*Decompositions.* 1. Phthalic acid volatilises completely when heated, and is resolved into water and anhydrous phthalic acid, the latter condensing in oily drops which solidify into a radiated crystalline mass on cooling. It burns on platinum foil with a smoky flame. (Schunck.) — 2. It is not decomposed by chlorine, hydrochloric acid, or nitric acid. — 3. On heating the acid with sulphuric acid, it evolves vapours without blackening; these vapours on condensing form white needles of the anhydride. (Schunck.) — 4. Heated with excess of caustic potash, it is decomposed into benzol and carbonic acid :



(Marignac, Schunck.) — 5. On boiling phthalic acid with hydrochloric acid and alcohol, a heavy oil is ultimately formed (phthalate of ethyl). (Laurent.)

*Combinations.* 1. The acid is but little soluble in water. It dissolves without decomposition in sulphuric, hydrochloric and nitric acids.

The *phthalates* are either *monobasic* (acid) =  $C^{16}H^8MO^8$ , or *bibasic* (neutral) =  $C^{16}H^8M^2O^8$ . Those of the alkalis are readily soluble in water and less in alcohol; the others are sparingly soluble or insoluble. When heated they become black, swell up, and yield a crystalline sublimate. Heated with sulphuric acid, they yield phthalic anhydride. (Laurent.) When heated, they emit an odour resembling that of benzol, yield a brown oil, and leave a residue of carbonate and charcoal. (Schunck.)

*Phthalate of Ammonia.* — The aqueous acid neutralised (or supersaturated) with ammonia and left to evaporate, yields crystals of the monobasic salt in the form of prisms belonging to the right prismatic system, together with 4 or 8-sided pyramids or 6-sided tablets.  $P. oP. \check{P}^\infty$ ;  $P : P = 133^\circ 50'$ ;  $oP : P = 112^\circ$ ;  $oP : \check{P}^\infty = 127$ ;  $\check{P}^\infty : \check{P}^\infty = 103^\circ 30'$ ; easily cleavable in the direction of  $oP$ . The salt does not give off water at  $120^\circ$ , but yields phthalimide when heated. It is readily soluble in water, but slightly in alcohol. (Laurent, Marignac.)

					Laurent.		Marignac.		
					a.	b.			
16 C	96	....	52.46	.....	52.1	....	51.16	....	52.39
N	14	....	7.65	.....	9.0	....	9.06	....	7.89
9 H	9	....	4.92	.....	4.9	....	4.95	....	4.94
8 O	64	....	34.97	.....	34.0	....	34.83	....	34.78
$C^{16}H^8(NH^4)O^8$ 183					100.0	....	100.00	....	100.00

In Laurent's analysis *a*, the acid was prepared according to No. 1; in *b*, according to No. 2.

*Phthalate of Potash* is obtained in small plates of pearly lustre by evaporating the solution to dryness and treating the residue with ether. It is very soluble in water. (Laurent.) Deliquescent crystalline mass. (Schunck.)

*Phthalate of Soda.* — The aqueous solution when left to evaporate becomes covered with a crust of crystals, which when dissolved in hot alcohol, yields small crystalline scales on cooling. The salt is readily soluble in water.



*Phthalate of Baryta* is precipitated in a few moments in white scales on mixing the concentrated neutral solution of the ammonia-salt with a concentrated solution of chloride of barium; it requires a considerable quantity of water for its solution. (Laurent.) Forms needles having a silky lustre. (Schunck.)

*Phthalate of Lime* is obtained by dissolving carbonate of lime in an aqueous solution of the acid. Similar to the baryta-salt. (Laurent, Schunck.)

The ammonia-salt does not precipitate salts of magnesia.

*Phthalate of Zinc* separates as a crystalline powder on evaporating the solution of carbonate of zinc in an aqueous solution of the acid. It is slightly soluble in water. Swells up when heated and yields an oil which crystallises on cooling.

*Phthalate of Lead.* — The aqueous solution of the acid forms with acetate of lead a white powder, not soluble in water or in acetic acid. (Schunck.) On mixing a boiling dilute solution of a lead-salt with phthalate of ammonia, silver-white scales separate out. (Laurent.)

					Schunck.
2 PbO .....	223.6	...	60.17	.....	61.44
16 C .....	96.0	...	25.83	.....	23.53
4 H .....	4.0	...	1.07	.....	1.49
6 O .....	48.0	...	12.93	.....	13.54
<hr/>					
$C^{16}H^4Pb^2O^8$ .....	371.6	...	100.00	.....	100.00

*Phthalate of Silver* separates in white shining scales on mixing the boiling solutions of nitrate of silver and phthalate of ammonia. (Laurent, Marignac.) It obstinately retains nitrate of ammonia. (Marignac.) Deflagrates when suddenly heated; when carefully heated, it melts, blackens and decomposes. (Laurent.) Moderately soluble in water. (Marignac.)

					Marignac.	Wolff and Strecker.	
						a.	b.
2 AgO .....	232	...	61.05	.....	61.02	...	60.99
16 C .....	96	...	25.26	.....	24.99	...	25.20
4 H .....	4	...	1.05	.....	1.20	...	1.15
6 O .....	48	...	12.64	.....	12.79	...	12.66
<hr/>							
$C^{16}H^4Ag^2O^8$ .....	380	...	100.00	.....	100.00	...	100.00

The salt *a.* analysed by Wolff & Strecker was prepared with the acid from alizarin ; *b.* with the acid from purpurin.

The acid is readily soluble in alcohol.

### Terephthalic Acid.



CAILLOT. (1847.) *N. Ann. Chim. Phys.* 21, 28; *J. pr. Chem.* 42, 233; *Pharm. Centr.* 1847, 201.

*Formation and Preparation.* Oil of turpentine is distilled with a large excess of a mixture of equal parts of nitric acid and water, till no



more red fumes are evolved; a resin is then formed, from which the acid mother-liquor is separated and evaporated down, and the residue is treated with cold water, which leaves behind an orange-yellow, pitchy mixture of resin, terephthalic acid and terebenzic acid. The latter may be removed by alcohol or by boiling water, and the terephthalic acid is separated from the residue by ammonia. The ammonia salt is purified by animal charcoal and recrystallisation, and precipitated by a mineral acid.

*Properties.* White tasteless crystalline powder.

				Caillot.
16 C .....	96	.....	57.84	..... 57.98
8 H .....	8	.....	3.61	..... 3.70
8 O .....	64	.....	38.55	..... 38.32
<hr/>				
$C^{16}H^8O^8$ .....	166	.....	100.00	..... 100.00

*Isomerie with phthalic acid.*

*Decompositions.* 1. Terephthalic acid evolves carbonic acid when heated — part of it however subliming undecomposed and completely saturated with benzol, — and leaves a small residue of carbon. — 2. Heated with hydrate of lime, it is completely resolved into carbonic acid and benzol.

*Combinations.* Terephthalic acid is insoluble in water.

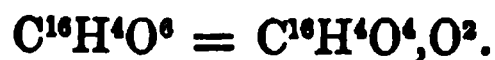
*Salts of Terephthalic Acid.* — The acid is perfectly soluble in alkalis, and neutralizes them completely (it is precipitated from the solution by phthalic acid). Almost all its salts are crystallisable; they are very combustible, and when well dried, may be ignited by the sparks of flint and steel, and burn like tinder, with a smell of benzol.

*Terephthalate of Silver.* — Obtained by precipitation. Dried at  $100^\circ$  it yields 56.6 per cent. silver on ignition (= 60.80 oxide), corresponding to the formula  $C^{16}H^4Ag^2O^8$ .

The acid is insoluble in alcohol and in ether.

*Oxygen-nucleus*  $C^{16}H^4O^4$ .

**Phthalic Anhydride.**



LAURENT. (1836). *Ann. Chim. Phys.* 61, 114; *Ann. Pharm.* 19, 38; *J. pr. Chem.* 8, 13; *Pharm. Centr.* 1836, 443.

MARIGNAC. *Ann. Pharm.* 42, 215; *N. Bibl. univ.* 36, 370.

*Anhydrous phthalic acid, Pyroalizaric acid.*

*Formation and Preparation.* By subliming phthalic acid in a Mohr's apparatus (p. 12).

*Properties.* Phthalic anhydride forms long white needles having the lustre of silk and united in feathery groups; their section forms a rhombus of  $152^\circ$  and  $128^\circ$ , like benzoic acid. Melts at  $105^\circ$  (Laurent), and solidifies in fibres; volatilises at higher temperatures in white suffocating vapours without leaving a residue. It is inodorous, and has a feeble taste which is not disagreeable.

				Laurent.	Marignac.	Schunck.
16 C .....	96	...	64.87	64.70	64.88	64.02
4 H .....	4	...	2.70	2.38	2.71	3.07
6 O .....	48	...	32.43	32.92	32.41	32.91
$C^{16}H^4O^6$ .....	148	...	100.00	100.00	100.00	100.00

*Reactions.* 1. Phthalic anhydride forms phthalic acid when boiled with water. — 2. It dissolves in ammonia, with evolution of heat, and yields phthalamic acid :



Insoluble in water.

*Bromine-nucleus*  $C^{16}BrH^7$ .

### Bromide of Styrol.



GERHARDT & CAHOUS. (1841.) *N. Ann. Chim. Phys.* 1, 96.

E. KOPP. *Compt. rend.* 21, 1878; *J. pr. Chem.* 37, 181; *Pharm. Centr.* 1847, 238.

BLYTH & HOFMANN. *Ann. Pharm.* 53, 305; *Pharm. Centr.* 1845, 410.

*Bromide of Cinnamene, Bromocinnamene.*

*Formation and Preparation.* When bromine is carefully added to cinnamene (Gerhardt & Cahours, E. Kopp), or to styrol (Blyth & Hofmann), the whole solidifies into a crystalline mass without evolving fumes of hydrobromic acid. A slight excess of bromine is added and the yellow mass is exposed for some time to the air until it becomes white; or it is pressed between paper and crystallised from alcohol or ether.

*Properties.* Bromide of styrol crystallises from ether in needles (Gerhardt & Cahours); and from a mixture of alcohol and ether, by spontaneous evaporation, in beautiful rhombic flakes; when rapidly cooled, it crystallises in fine needles. (E. Kopp.) It cannot be obtained in well defined crystals from alcohol or ether. (Blyth & Hofmann.) Has a peculiar aromatic odour, which is not unpleasant, but irritates the eyes and excites tears (E. Kopp); has a peculiar penetrating odour reminding one both of oil of lemons and of oil of juniper. (Blyth & Hofmann.) Melts at  $67^\circ$  and on cooling often remains fluid at  $30^\circ$ , but solidifies on the slightest agitation. (E. Kopp.) Melts in boiling water. (Blyth & Hofmann.) Boils at  $230^\circ$  and distils wholly without decomposition. (E. Kopp.)

16 C .....	96 .....	36.36 .....	36.55 .....	36.23
2 Br .....	160 .....	60.61 .....	.....	59.83
H .....	8 .....	3.03 .....	3.04 .....	3.18
<hr/>				
$C^{16}Br^2H^8$ .....	264 .....	100.00 .....	.....	99.24

*Decompositions.* On treating bromide of styrol with nitric acid, it loses all its bromine and is converted into a crystallisable substance which appears to be nitrobenzoic acid. (E. Kopp.) With an alcoholic solution of potash, it forms bromide of potassium and a bromine-compound which appears to be  $C^{16}BrH^7$ . (Gerhardt & Cahours, E. Kopp, Blyth & Hofmann.)

*Combinations.* Bromide of styrol is not soluble in water, but nevertheless imparts to it its taste and smell. It is readily soluble in alcohol and mixes in all proportions with ether. On cooling its boiling alcoholic solution, it separates out as a heavy oil, which also remains liquid on cooling, but suddenly solidifies when shaken. (Blyth & Hofmann.)

#### *Chlorine-nucleus $C^{16}ClH^7$ .*

#### Chloride of Styrol.



BLYTH & HOFMANN. (1845.) *Ann. Pharm.* 53, 309; *Pharm. Centr.* 1845, 411.

LAURENT. *Compt. rend.* 22, 790.

Chlorine is slowly passed through styrol, which is kept cool, in the shade, till hydrochloric acid begins to be evolved. As an excess of chlorine gives rise to the replacement of hydrogen in the styrol by chlorine, it is difficult to obtain the compound pure. (Blyth & Hofmann.)

Chloride of styrol forms a thick liquid which smells and tastes like the bromide.

				Blyth & Hofmann.
16 C .....	96 .....	54.92 .....	.....	55.26
8 H .....	8 .....	4.57 .....	.....	4.70
2 Cl .....	70.8 .....	40.51 .....	.....	
<hr/>				
$C^{16}H^8Cl^2$ .....	174.8 .....	100.00 .....	.....	

Decomposes when heated, evolving hydrochloric acid and forming an oil which appears to be  $C^{16}ClH^7$ . This oil is formed in large quantities by distilling chloride of styrol over quick lime. (Blyth & Hofmann.)

On treating chloride of styrol with potash,  $C^{16}ClH^7$  is formed. (Laurent.) Heated with alcoholic potash, it yields a heavy fragrant oil, which strongly excites tears. It is decomposed by distillation, giving off

copious fumes of hydrochloric acid, but yields a colourless distillate when distilled with steam. It yielded 18.58 p. c. chlorine, the formula of chlorostyrol  $C^{16}ClH^7$  requiring 25.58 p. c. When this oil is covered with a thin film of water and exposed to the air, the water soon becomes acid from the presence of hydrochloric acid, and crystalline laminæ separate, consisting of benzoic acid. (Kubel, *Ann. Pharm.* 102, 238.) According to Laurent, a compound also exists in which 2 At. H are replaced by 8 At. Cl;— $C^{16}H^6Cl^8 = C^{16}Cl^8H^6,Cl^6$ .

*Oxychlorine-nucleus*  $C^{16}Cl^3H^4O^2$ .

### Bichlorophthalic Acid.



WOLFF & STRECKER. (1850.) *Ann. Pharm.* 75, 16.

Bichlorophthalic acid was once obtained from naphthalin together with a chloronaphthalic acid containing from 2 to 3 atoms of chlorine. Silvery flakes are precipitated from the alcoholic solution on neutralising with potash.

			At 140°.	Wolff & Strecker.
16 C	.....	96	..... 80.85	..... 30.04
2 Cl	.....	70.8	..... 22.75	
2 H	.....	2	..... 0.64	..... 0.7
2 K	.....	78.4	..... 25.19	..... 24.3
8 O	.....	64	..... 20.57	
$C^{16}Cl^2H^2K^2O^8$ ....			311.2	..... 100.00

*Oxychlorine-nucleus*  $C^{16}Cl^3H^3O^2$ .

### Terchlorophthalic Acid.



LAURENT. (1843.) *Rev. scient.* 13, 603.

When *sexchloronaphthalin* is boiled for several days with nitric acid and the product mixed with water, a resinous mass separates out, and the solution yields, after evaporation, a crystalline magma of terchlorophthalic acid, which, after being repeatedly pressed between blotting paper and recrystallised from boiling water, yields crystalline grains. It is very easily soluble in boiling water, alcohol and ether. When heated, it is resolved into water and anhydrous terchlorophthalic acid. The ammonia salt forms a white precipitate with salts of silver.

*Oxychlorine-nucleus*  $C^{16}Cl^1HO^4$ .

### Terchlorophthalic Anhydride.



LAURENT.

Obtained by the dry distillation of terchlorophthalic acid. It is colourless and solidifies in needles after fusion. With ammonia it forms a compound which gives a white precipitate with silver salts.

*Nitro-nucleus*  $C^{16}XH^7$ .

### Nitrostyrol.



E. SIMON. (1839.) *Ann. Pharm.* 31, 266; *Pharm. Centr.* 1839, 858.

BLYTH & HOFMANN. *Ann. Pharm.* 53, 297; *Pharm. Centr.* 1845, 408.

*Formation.* (p. 4).

*Preparation.* 1. Styrol is distilled with common nitric acid till it is completely converted into a brown resin; this is washed and distilled with water, nitrostyrol passing over with the vapour of water. (Simon.) If the distillation is too long protracted, benzoic acid may pass over. Very little nitrostyrol is obtained. (Blyth & Hofmann, compare p. 4.) — 2. When styrol is added drop by drop to fuming nitric acid, water precipitates from the solution a soft yellow resin, which, if washed with cold water and then distilled with water, yields rather more nitrostyrol than when a weaker acid is employed. (Blyth & Hofmann.)

*Properties.* Nitrostyrol crystallises from alcohol in prisms belonging to the right prismatic system  $\infty P. \infty \bar{P} \infty. \infty \bar{P} \infty. \bar{P} \infty$  with predominating faces  $\infty \bar{P} \infty$ ;  $\infty P \infty : P (\alpha : \alpha') = 97^\circ$ . (G. Rose.) It smells very strongly of oil of cinnamon, but has a much sharper taste; provokes tears and raises blisters on the skin, like oil of mustard. Passes over as an oil with vapour of water.

				Blyth & Hofmann.	
16 C .....	96	.....	64.43	.....	64.27
N .....	14	.....	9.39	.....	10.30
7 H .....	7	.....	4.70	.....	5.11
4 O .....	32	.....	21.48		
<hr/>					
$C^{16}NH^7O^4$ .....	149	.....	100.00		

On distilling nitrostyrol with an alcoholic solution of potash, reddish-yellow drops pass over with the alcohol, consisting of an oil which

appears to be analogous to azobenzide. An attempt to prepare a base from it by means of sulphide of ammonium was not successful. (Blyth & Hofmann.)

Nitrostyrol is soluble in boiling alcohol, but crystallises out on cooling.

### Nitrometastyrol.



GLÉNARD & BOUDAULT. (1844.) *Compt. rend.* 19, 509; *N. J. Pharm.* 6, 257; *J. pr. Chem.* 33, 466.

BLYTH & HOFMANN. *Ann. Pharm.* 53, 316; *Pharm. Centr.* 1845, 425

#### Formation (p. 7).

*Preparation.* Metastyrol is dissolved in a quantity of boiling fuming nitric acid just sufficient to keep it in solution when cold; the solution is precipitated with water, and the white curdy mass thus obtained is washed with water, and then with alcohol, in order to remove any benzoic acid that may be mixed with it. If too little nitric acid is employed, a slimy mass separates from the solution on cooling, containing undecomposed metastyrol, which remains behind on treating the substance with sulphuric acid; if the boiling is carried too far, the nitric acid forms other products of decomposition (compare p. 7).

*Properties.* White or yellowish amorphous powder.

				Blyth & Hofmann.	
16 C .....	96	...	64.43	.....	61.32
N .....	14	...	9.39	.....	10.06
7 H .....	7	...	4.70	.....	4.71
4 O .....	32	...	21.48	.....	23.91
<hr/>					
$C^{16}NH^7O^4$ .....	149	...	100.00	.....	100.00

It probably contained binitrometastyrol (Blyth & Hofmann).

*Decompositions.* 1. Nitrometastyrol burns with slight deflagration when gently heated (Glénard & Boudault), exhaling a powerful odour of oil of bitter almonds. (Blyth & Hofmann.)—2. On heating it with quick lime, much carbon separates out, ammonia being evolved, and a brown oil containing aniline passing over. (Blyth & Hofmann.)

It is insoluble in water, alcohol and ether.

### Nitrophthalin.



L. DUBART. *N. Ann. Chim. Phys.* 44, 382; *Chem. Centr.* 1856, 7.

*Formation.* By the action of potash on nitronaphthalin:



**Preparation.** 2 pts. of caustic potash dissolved in as little water as possible are mixed with 1 pt. of fresh slaked lime, to which nitronaphthalin is gradually added. The action begins almost immediately, the mixture becoming reddish. The mass is kept for about 6 hours at a temperature not exceeding  $100^\circ$ , and is stirred from time to time, the evaporated water being replaced; the whole is then added to a large quantity of water and allowed to settle down; the alkaline solution, coloured deep yellow by nitrophthalic acid, is decanted off; and the deposit is washed with water until the latter is only slightly coloured. The lime is removed from the brown residue by dilute hydrochloric acid, and the remainder thrown on a filter and washed with water. The nitrophthalin can only be separated from the brown matter with which it is mixed by distilling with steam; it then passes over in oily drops which crystallise on cooling. If distilled alone the product is less pure.

**Properties.** Nitrophthalin is of a straw yellow colour and very crystalline. It crystallises on cooling from hot alcohol in long needles, which are tasteless and have a feeble odour. Melts at  $48^\circ$ , begins to boil at  $280^\circ$  and distils over in large quantities between  $300^\circ$  and  $320^\circ$ , leaving a slight carbonaceous residue.

				Dusart.
16 C .....	96	...	64.43	63.94
N .....	14	...	9.39	10.20
7 H .....	7	...	4.70	4.79
4 O .....	32	...	21.48	21.07
<hr/>				
$C^{16}NH^7O^4$ .....	149	...	100.00	100.00

Isomeric with nitrostyrol.

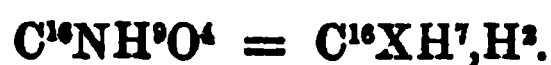
**Decompositions.** 1. Nitrophthalin leaves, when distilled, a small residue rich in carbon, resembling sugar-charcoal, which dissolves to a considerable extent in sulphuric acid, from which it is precipitated by water in dirty red flakes, slightly soluble in alcohol but imparting to it a reddish colour; this substance heated by itself in a tube, yields a red oil, which crystallises on cooling, and a large quantity of charcoal. — 2. Dissolves in sulphuric acid and imparts to it a red colour. — 3. Forms nitrophthalic acid when heated with a strong solution of potash, but not so readily with hydrate of lime or baryta. When distilled with dry potash-lime, it evolves a considerable quantity of ammonia, while an odorous oil distils over, and the sides of the retort become covered with long yellow needles which dissolve in sulphuric acid with a beautiful violet-blue colour. The oil is slightly soluble in water, and the solution gives with ferric salts an indigo-blue precipitate. — 4. With sulphide of ammonium it forms phthalidine, sulphur separating out:



**Combinations.** Nitrophthalin is not soluble in cold water; when distilled with water, it imparts to it an aromatic odour and separates on cooling in needles having a silky lustre.

It is but slightly soluble in cold *alcohol*, but readily in hot alcohol; dissolves abundantly in *ether* and in *coal-oil*.

## ¶. Phthalamine.



P. SCHUTZENBERGER & E. WILLM. *Compt. rend.* 47, 82; *Chem. Gaz.* 1858 343; *Repertoire de Chimie pure*, 1, 38.

When crude naphthylamine, obtained by the action of ferrous acetate on nitronaphthalin is treated with sulphuric acid, two sulphates are obtained, differing in their degree of solubility in water. The less soluble is sulphate of phthalamine, which crystallizes in nacreous scales, and gives off 8.06 to 8.15 p. c. water (2 At.) at 140°.

<i>Dried at 140°.</i>				Schutzenberger & Willm.	
16 C	.....	96	.... 48.0	.....	48.19
9 H	.....	9	.... 4.5	.....	5.22
N	.....	14	.... 7.0	.....	7.05
SO <sup>4</sup> H	.....	49	.... 24.5	.....	24.25
4 O	.....	32	.... 16.0	.....	15.29
<hr/>					
C <sup>16</sup> NH <sup>9</sup> O <sup>4</sup> , SO <sup>4</sup> H.....	200	....	100.0	.....	100.00

On adding ammonia to the solution of this salt, the base is precipitated in oily drops a little heavier than water. It has the taste of naphthylamine; its salts do not redden by exposure to the air.

## Ethyl-phthalamine.



SCHUTZENBERGER & WILLM. *loc. cit.*

When a solution of phthalamine is heated to 100° with iodide of ethyl, iodide of ethylphthalamine separates in a few minutes in foliated crystals, easily purified by crystallisation from water or alcohol. They are anhydrous and become green if exposed to the air while moist.

				Schutzenberger & Willm.	
20 C	.....	120	.... 39.22	.....	39.42
13 H	.....	13	.... 4.25	.....	4.5
N	.....	14	.... 4.57	.....	
I	.....	127	.... 41.51	.....	40.8
4 O	.....	32	.... 10.45	.....	
<hr/>					
C <sup>20</sup> NH <sup>13</sup> O <sup>4</sup> , I	.....	306	....	100.00	

Ammonia separates the base in the form of an oily liquid which boils at about 300°, is alterable in the air, and has a burning taste. ¶



**Nitrotoluylic Acid.**

NOAD. (1847.) *Phil. Mag. J.* 32, 25; *Mem. Chem. Soc.* 3, 431; *Ann. Pharm.* 63, 497; *Pharm. Centr.* 1848, 180.

**Formation.** By boiling cymol with the strongest fuming nitric acid (if weaker acid is employed, a neutral crystalline body is formed, which cannot easily be converted into nitrotoluylic acid) (Noad); or by heating with a mixture of nitric and sulphuric acids. (Kraut.)

**Preparation.** 1. Cymol is distilled with the strongest fuming nitric acid as long as red fumes are evolved. The residue deposits a large quantity of crystals on cooling, and gives a considerable precipitate when treated with water; the whole mass is washed on a filter with cold water, then digested with ammonia and filtered, whereby a little oily matter is separated. The filtrate is decomposed with hydrochloric acid; the precipitated nitrotoluylic acid washed with water, dried, dissolved in hot alcohol, and boiled with animal charcoal; and the filtrate is abandoned to spontaneous evaporation.

**Properties.** Nitrotoluylic acid forms beautiful pale yellow rhombic prisms.

					Noad.
16 C .....	96	...	53.04	.....	52.90
N .....	14	...	7.74	.....	7.96
7 H .....	7	...	3.87	.....	4.00
8 O .....	64	...	35.35	.....	35.14
<hr/>					
$C^{16}NH^7O^8$ .....	181	...	100.00	.....	100.00

The acid is not changed by several days' digestion with nitric and sulphuric acids.

**Combinations.** Nitrotoluylic acid is but slightly soluble in cold water.

*Nitrotoluylate of Ammonia* forms long needles; it loses all its ammonia by boiling with animal charcoal.

*Nitrotoluylate of Potash* crystallises with difficulty in small needles, and is very soluble.

The *Soda-salt* cannot be obtained crystallised.

*Nitrotoluylate of Baryta.* The ammonia salt forms, with chloride of barium, a white curdy precipitate, which dissolves abundantly in hot water, and separates out on cooling in needles united in the form of stars, which become lustrous when dry, and after recrystallisation contain 30.54 per cent. BaO, corresponding to the formula  $C^{16}XH^7BaO^4$ .

*Nitrotoluylate of Strontia* is prepared like the baryta salt, which it very much resembles, excepting that the crystals are larger and more readily soluble in water.

*Nitrotoluylate of Lime* is precipitated in the crystalline state from the ammonia salt by a solution of chloride of calcium; it is more soluble in water than the baryta salt, and crystallises in oblique rhombic prisms. It contains 14.27 per cent. of lime, corresponding to the formula  $C^{16}XH^{16}CaO^4$ .

*Nitrotoluylate of Copper*. — Sulphate of copper forms, with the perfectly neutral ammonia salt, a precipitate which is a basic salt.

*Nitrotoluylate of Silver*. — Nitrate of silver forms, with the ammonia salt, a curdy precipitate, very similar to chloride of silver, which dissolves abundantly in boiling water (if too long boiled it blackens); the solution, on cooling, deposits feathery crystals, which are but slightly soluble in alcohol.

					Noad.
16 C .....	96	...	33.33	.....	33.00
N .....	14	...	4.86	.....	
6 H .....	6	...	2.08	.....	2.12
Ag.....	108	...	37.51	.....	37.45
8 O .....	64	...	22.22	.....	
<hr/>					
$C^{16}NH^6AgO^8$ ....	288	...	100.00	.....	

Nitrotoluylic acid is soluble in hot alcohol.

### Nitrodracylic Acid.



GLÉNARD & BOUDAULT. (1844.) *N. J. Pharm.* 6, 255.

*Formation.* (xii, 229.)

*Preparation.* Toluol (dracyl) is distilled with a large quantity of fuming nitric acid till about three-fourths has passed over; on cooling, a crystalline mass separates out from the residue, soluble in hot water, while nitrotoluol sinks to the bottom of the vessel. The nitrodracylic acid is obtained pure by repeated recrystallisation,

*Properties.* White, slender, shining needles, grouped together in very light stars. When heated on platinum foil, it volatilises with a strong penetrating odour, leaving a scarcely perceptible carbonaceous residue, and sublimes in fine needles.

					Glénard & Boudault.
16 C .....	96	...	53.05	.....	52.34
N .....	14	...	7.73	.....	8.00
7 H .....	7	...	3.86	.....	3.46
8 O .....	64	...	35.36	.....	36.20
<hr/>					
$C^{16}NH^7O^8$ .....	181	...	100.00	.....	100.00

Glénard & Boudault assume the formula  $C^{16}NH^6O^4$  (it is perhaps nitrobenzoic acid containing nitrostyrol. L.).

**Combinations.** Nitrodracylic acid is insoluble in cold, and slightly soluble in hot, water; the solution begins to crystallise at  $70^\circ$ , and at  $60^\circ$  the greater part of the acid is separated out. The acid liberates carbonic acid from its compounds; the solutions of its salts are decomposed by strong acids; and from concentrated solutions, the nitrodracylic acid is precipitated as a white amorphous mass. The salts melt on ignited charcoal.

The nitrodracylates of the alkalis are formed by direct combination, and are very soluble; the other salts are formed by double decomposition, or by boiling the acid with an oxide or carbonate.

Nitrodracylic acid gives, with ferrous salts, a white precipitate, which becomes red on boiling; it does not precipitate ferric salts.

*Nitrodracylate of Copper* is a green powder, soluble in water and in alcohol.

*Nitrodracylate of Lead* crystallises in shining white radiating needles; it is moderately soluble in water, and contains 38.50 per cent. oxide of lead.

*Nitrodracylate of Silver* crystallises in nodules, and dissolves with tolerable facility in water.

The acid is very soluble in alcohol.

### Nitrotoluylate of Methyl.



Noad.

When a solution of nitrotoluylic acid in methylic alcohol is saturated with hydrochloric acid gas and distilled, the methyl-compound remains in the retort as an oil coloured black by the products of decomposition of the wood-spirit. The oil is washed with water, and solidifies in the course of a few hours, but cannot be purified by distilling with water, on account of its high boiling point. If it is dissolved in strong nitric acid and boiled for a few minutes, a clear yellow oil is precipitated from the solution on the addition of water; and this oil, after being washed with water containing ammonia, soon solidifies into a crystalline mass, which is recrystallised from ether and dried over the water-bath.

**Properties.** Water distilled off nitrotoluylate of methyl deposits it in colourless needles united in stellate groups. Its odour is not so agreeable as that of the ethyl-compound.

				Noad.
18 C .....	108	...	55.38	54.84
N .....	14	...	7.18	
9 H .....	9	...	4.61	4.83
8 O .....	64	...	32.83	
<hr/>				
$C^{10}NH^1O^3$ .....	195	...	100.00	

Splits up, when treated with alcoholic solution of potash into wood-spirit and the potash-salt.

**Nitrotoluylate of Ethyl.****Noad.**

The alcoholic solution of the acid saturated with hydrochloric acid gas is distilled until the mixture of hydrochloric acid and alcohol begins to show turbidity with water. The oil remaining in the retort then solidifies to a crystalline mass, which, after being washed with carbonate of potash and then with water, is dried between blotting-paper.

*Properties.* Melts in the water-bath and forms a clear liquid, which on cooling solidifies into a radiated crystalline mass. It has a pleasant odour.

				Noad.
20 C .....	120	...	57.42	..... 57.26
N .....	14	...	6.69	
11 H .....	11	...	5.26	..... 5.37
8 O .....	64	...	30.63	
<hr/>				
$\text{C}^{\text{20}}\text{NH}^{\text{11}}\text{O}^{\text{8}}$ .....	209	...	100.00	

It is decomposed by potash into alcohol and the potash-salt. Does not form nitrotoluylamide with ammonia.

*Nitro-nucleus*  $\text{C}^{\text{16}}\text{X}^{\text{3}}\text{H}^{\text{5}}$ .

**Nitrococcusic Acid.**

WARREN DE LA RUE. (1847.) *Mem. Chem. Soc.* 3, 469; *Ann. Pharm.* 64, 23; *Pharm. Centr.* 1848, 86.

*Formation and Preparation.* 3 pts. of carminic acid are gradually added to 20 pts. of warm nitric acid of sp. gr. 1.4, whereupon a violent evolution of nitrous acid takes place. When all the acid has been added and the action diminishes, the solution is kept boiling for two hours, during which the greater part of the nitric acid evaporates; the solution on cooling becomes thickened with crystals of nitrococcusic acid and oxalic acid. The crystals are dissolved in boiling water and the oxalic acid precipitated by nitrate of lead. The yellow filtrate deposits more oxalate of lead on evaporation, and on cooling yields rhombic prisms of nitrococcusic acid, which are pressed and repeatedly recrystallised from boiling water. Carminate of lead may be employed instead of carminic acid.

*Properties.* Nitrococcusic acid crystallises in beautiful yellow rhombic tablets, containing 2 atoms of water of crystallisation (5.96 per cent.) which are driven off at  $100^\circ$ . The solution stains the skin yellow.

					Warren de la Rue.
16 C .....	96	...	33.45	.....	33.75
3 N .....	42	...	14.63	.....	14.97
5 H .....	5	...	1.74	.....	1.91
18 O .....	144	...	50.18	.....	49.37
<hr/> $C^{16}N^3H^5O^{18}$ .... 287					100.00
					..... 100.00

Isomerie with nitrosalleylate of methyl and ternitroanisic acid.

*Decompositions.* 1, Nitrococcusic acid boiled with water and oxide of silver, evolves large quantities of carbonic acid; the solution when heated gives a brown precipitate, and the filtrate yields, on evaporation, a silver salt containing 38.10 per cent. AgO, 23.64 per cent. C, and 1.26 per cent. H. This salt decomposed by hydrochloric acid yields an acid crystallising in long needles, slightly soluble in water, and readily soluble in alcohol and in ether. — 2. Aqueous solution of nitrococcusic acid dissolves iron and zinc with evolution of hydrogen, and becomes more deeply coloured. — 3. It is converted into another acid by sulphide of ammonium, sulphur separating out.

*Combinations.* Nitrococcusic acid is much more soluble in hot water than in cold.

The salts of nitrococcusic acid are yellow, for the most part soluble in water and also in alcohol; they deflagrate very violently when heated.

*Nitrococcusate of Ammonia.* — When gaseous ammonia is passed through the ethereal solution of the crystallised acid, tufts of crystalline needles are deposited on the sides of the vessel; they are washed with ether and dried between folds of paper. The salt sublimes when heated, but probably not without decomposition.

					Warren de la Rue.
16 C .....	96	...	29.09	.....	29.05
5 N .....	70	...	21.21	.....	
12 H .....	12	...	3.64	.....	3.97
19 O .....	152	...	46.06	.....	
<hr/> $C^{16}N^3H^5(NH^4)^2O^{18} + Aq$ .....					330
					100.00

					Warren de la Rue.
2 $NH^4O$ .....	52	...	15.76	.....	15.91
$C^{16}N^3H^5O^{18}$ .....	269	...	81.51	.....	
HO .....	9	...	2.73	.....	
<hr/> $C^{16}N^3H^5(NH^4)^2O^{18} + Aq$ .....					330
					100.00

*Nitrococcusate of Potash.* — 1. The aqueous solution of the acid is carefully neutralised with carbonate of potash, the solution evaporated, and left to cool, and the crystals thus obtained are purified by recrystallisation. — 2. The solution of the acid in ether is carefully precipitated by a solution of potash in alcohol; the pale yellow precipitate is washed with ether, dried, dissolved in as little cold water as possible; and the

solution is mixed with 5 times its volume of absolute alcohol; it then after a while deposits well-defined crystals (still more on the addition of ether), which are washed with ether and dried.

	At 100°.		Warren de la Rue,
2 KO .....	94.4	25.89	25.83
16 C .....	96	26.45	26.46
3 N .....	42	11.57	
3 H .....	3	0.83	1.18
16 O .....	128	35.26	
<hr/>			
$C^{16}N^3H^3K^2O^{18}$ .....	363.4	100.00	

No acid salt is obtained by mixing the solution with free nitrococcusic acid.

*Nitrococcusate of Baryta.* — The acid is dissolved in baryta water; carbonic acid passed through the solution, which is then warmed and filtered; the filtrate is concentrated on a water-bath; and the solution is again filtered, to remove traces of carbonate of baryta, evaporated till it begins to crystallise on the surface, and left to cool. Small yellow crystals, insoluble in alcohol.

*Nitrococcusate of Copper.* — The solution of carbonate of copper in the aqueous solution of the acid yields pale apple-green crystals on evaporation.

*Nitrococcusate of Silver.* — Oxide of silver is dissolved in the cold aqueous solution of the acid, and the filtrate evaporated in vacuo over sulphuric acid. Long bulky yellow needles, which become orange-yellow at 100°. Deflagrates with great violence a little above 200° when rapidly heated, but decomposes without deflagrating when gradually heated in small quantities. It is soluble in water and in alcohol.

			Warren de la Rue.
2 AgO .....	232	46.31	46.00
16 C .....	96	19.16	18.99
3 N .....	42	8.38	
3 H .....	3	0.60	0.75
16 O .....	128	25.55	
<hr/>			
$C^{16}N^3H^3Ag^2O^{18}$ .....	501	100.00	

Nitrococcusic acid dissolves in alcohol, and very readily in ether.

*Oxyntro-nucleus*  $C^{16}XH^5O^3$ .

**Nitrophthalic Acid.**

$C^{16}NH^5O^{12} = C^{16}XH^5O^3, O^9$ .

LAURENT (1840.) *Rev. scient.* 6, 88; *Ann. Pharm.* 41, 104; *Rev. scient.* 9, 81; 12, 602; *Compt. rend.* 31, 529.  
MABIGNAC. *Ann. Pharm.* 38, 1.

*Nitronaphthalic acid, Nitronaphtalesic acid.*

**Formation.** By the prolonged action of nitric acid upon naphthalin.

*Preparation.* 1. The crystals obtained in the preparation of phthalic acid from naphthalin are several times recrystallised. (Laurent, p. 11.) — 2. Naphthalin is distilled with nitric acid in a tubulated retort for several days, fresh nitric being added when no more red vapours are evolved. The residue is treated every evening with water, in order to remove the small quantity of nitrophthalic acid which has been formed; the solution is evaporated to dryness, in order to purify the acid from resinous matter; and the residue is treated with a little cold water, which, by means of the small quantity of unevaporated nitric acid still present, dissolves out the resin, and leaves the greater part of the acid undissolved, as a yellow powder, which is recrystallised several times from boiling water. — Or the aqueous extract is shaken up with ether, which dissolves the resin; the aqueous solution is left to evaporate; and the residue is purified by recrystallisation. (Marignac.)

*Properties.* Nitrophthalic acid forms pale yellow crystals belonging to the oblique prismatic system, which form rhomboidal tablets, generally converted into six-sided tablets by truncation of the acute angles. Fig. 106.  $i : u = 104^\circ$ ;  $u : u = \text{about } 125^\circ$ ;  $i : t = 124^\circ$ ; commonly with hemihedral development. The crystals deposited from the aqueous solution have strongly striated faces.

						Laurent.	Marignac.
16 C	.....	96	....	45.50	.....	45.68	.... 45.43
N	.....	14	....	6.63	.....	6.70	.... 6.63
5 H	.....	5	....	2.37	.....	2.59	.... 2.53
12 O	.....	96	....	45.50	.....	45.03	.... 45.41
<hr/>							
C <sup>16</sup> NH <sup>5</sup> O <sup>12</sup>	.....	211	....	100.00	.....	100.00	.... 100.00

*Decompositions.* 1. Nitrophthalic acid when carefully heated splits up into water and nitrophthalic anhydride. (Marignac.) — 2. If rapidly heated, it melts, swells up, and evolves water and a little nitrophthalic anhydride; the residue becomes coloured, evolves nitrous fumes, and finally decomposes, leaving suddenly an abundant residue of charcoal; very rapid heating sometimes causes deflagration. (Laurent, Marignac.) — 3. When the lead-salt is suspended in water and decomposed by sulphuretted hydrogen, the colourless filtrate becomes quite inodorous if gently heated, and only slightly turbid from precipitation of sulphur; after a time (immediately on boiling) a body separates out, insoluble in water, hydrochloric acid, alcohol, and ether, soluble in potash with dark brown colour, and precipitated from its solution by acids. — If the aqueous solution of the acid, while yet colourless and no longer smelling of sulphuretted hydrogen, is mixed with acetate of lead, a whitish precipitate is formed, which when dry, deflagrates by heat, and contains  $C^{16}NH^9O^9, 3PbO$ . (Marignac.)

*Combinations.* Nitrophthalic acid dissolves slightly in cold water but with tolerable facility in boiling water. (Laurent, Marignac.)

Nitrophthalic acid forms *monobasic* (acid) salts =  $C^{16}XH^4MO^8$ , and *bibasic* (neutral) salts =  $C^{16}XH^3M^2O^8$ .

*Nitrophthalate of Ammonia.* a. *Monobasic.* — The solution of the acid in ammonia deposits, by spontaneous evaporation, remarkably brilliant flakes of the monobasic salt, with which a few smaller and thicker

crystals of the neutral salt are sometimes mixed. The monobasic salt ( $C^{16}XH^4(NH^4)O^6$ ) is also formed by acidifying the solution of the neutral salt with nitric acid. It generally forms prisms terminated by pyramids, or rhomboidal, or six-sided tables. Does not give off any water at  $120^\circ$ .

*b. Bibasic.* The neutral salt crystallises in oblique rhombic prisms, the obtuse edges being generally truncated. (Fig. 81),  $i : u = 130^\circ$ ;  $u : u =$  about  $127^\circ$ . It evolves nitrophthalic acid when heated, and forms a peculiar compound with dry gaseous ammonia. (Laurent.)

					Laurent.
16 C .....	96	...	39.18	.....	39.33
3 N .....	42	...	17.15	.....	17.70
11 H .....	11	...	4.49	.....	4.73
12 O .....	96	...	39.18	.....	38.24
<hr/>					
$C^{16}NH^3(NH^4)O^{12}$ ....	245	...	100.00	.....	100.00

*Nitrophthalate of Baryta* is produced by boiling carbonate of baryta with even an excess of acid as an insoluble yellow powder, which, when dried at  $100^\circ$  is free from water, and deflagrates when strongly heated. It contains 44.28 per cent. baryta, corresponding to the formula  $C^{16}XH^3Ba^2O^6$ . (Marignac.)

The ammonia-salt also forms a white precipitate with a dilute boiling solution of chloride of barium. The precipitates with salts of strontia and lime are somewhat more soluble. (Laurent.)

*Nitrophthalate of Lead.* — No neutral salt can be obtained. (Marignac.) — *Basic.* The ammonia-salt forms, with acetate of lead, a flocculent precipitate, which is converted into a yellowish powder on boiling. It is insoluble in water, and deflagrates when heated. (Marignac.)

					Marignac.
4 PbO .....	447.2	...	69.85	.....	69.56
16 C .....	96	...	14.99	.....	15.07
3 N .....	14	...	2.19	.....	
3 H .....	3	...	0.47	.....	0.54
10 O .....	80	...	12.50	.....	
<hr/>					
$C^{16}NH^3Pb^2O^{12}, 2PbO$ ....	640.2	...	100.00	.....	

*Nitrophthalate of Silver* is obtained by precipitating nitrate of silver with the ammonia-salt. It forms a white powder, which, when heated, deflagrates suddenly, with emission of light (Laurent, Marignac); when very carefully heated, it melts and decomposes without explosion. (Laurent.)

					Laurent.	Marignac.
16 C .....	96	...	22.59	.....	...	22.56
3 N .....	14	...	3.29	.....	...	2.85
3 H .....	3	...	0.71	.....	...	0.86
2 Ag .....	216	...	50.82	.....	50.00	49.64
12 O .....	96	...	22.59	.....	...	24.09
<hr/>						
$C^{16}NH^3Ag^2O^{12}$ ....	425	...	100.00	.....	...	100.00

Nitrophthalic acid is very soluble in *alcohol* and in *ether*.



*Oxyamidogen-nucleus*  $C^{10}AdH^2O^2$ .**Phthalamie Acid.**

MARIGNAC. (1842.) *Ann. Pharm.* 42, 219; *N. Bibl. univ.* 36, 370.

LAURENT. *N. Ann. Chim. Phys.* 23, 117; *J. pr. Chem.* 45, 174.

*Phthalamide. Naphthalamide.*

*Formation.* (p. 15.)

Phthalamie acid is not known in the free state, since it takes up water on evaporating and forms acid phthalate of ammonia:



*Phthalamate of Ammonia.* — When the alcoholic solution of phthalic anhydride is treated with caustic ammonia, crystals of phthalamate of ammonia separate on cooling. Small colourless prisms bevelled with two terminal faces. It is very soluble in water, and soluble in alcohol. (Laurent.)

				Laurent.
	NH <sup>2</sup> .....	17	...	9.84 .....
16 C	.....	96	...	52.74 .....
N	.....	14	...	7.69 .....
7 H	.....	7	...	3.85 .....
6 O	.....	48	...	26.38 .....
<hr/>				
	$C^{10}NH^2(NH^4)O^2$ .....	182	...	100.00

The acid needles having an acid reaction, obtained by Marignac from the solution of phthalic anhydride in caustic ammonia, which he calls *naphthalamide*, and whose analysis led to the formula  $C^{10}NH^2O^2$ , must have been phthalamate of ammonia, partly converted into phthalimide (Laurent).

The salt dissolved in a small quantity of water and mixed with alcohol and bichloride of platinum, immediately yields a quantity of chloroplatinate of ammonium corresponding to 1 atom of ammonia; the filtrate, boiled with excess of bichloride of platinum, yields about the same quantity of chloroplatinate of ammonium. When the aqueous solution of phthalamate of ammonia is boiled for some time, it gives off water and ammonia, and is converted into phthalimide:

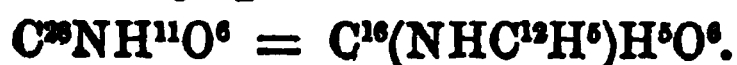


The aqueous solution of phthalamate of ammonia forms, with acetate of lead, a precipitate, which, when decomposed by sulphuretted hydrogen, and filtered, yields crystals of acid phthalate of ammonia by evaporation. (Laurent.)

*Phthalamate of Silver.* — A solution of phthalamate of ammonia in boiling alcohol does not at first form a precipitate with a concentrated

solution of nitrate of silver; but in a few minutes the solution becomes filled with fine needles. On treating the crystals with hot water, they dissolve, but the phthalate of ammonia gives off 2 atoms of water, and the solution deposits very brilliant flakes, which contain 40.2 per cent. Ag, and consist of a compound of phthalimide with argentammonium ( $C^{16}NH^4(NAgH^3)O^4$ .) (Laurent.)

### Phenyl-phthalamic Acid.\*



LAURENT & GERHARDT. (1848.) *N. Ann. Chim. Phys.* 24, 190.

#### *Phthalanilic acid.*

Phenyl-phthalamide is boiled with ammonia and a little alcohol, till in the course of a few minutes the whole is dissolved, and the solution, while still hot, is neutralised with nitric acid. The acid crystallises out on cooling.

It forms beautiful crystalline flakes; melts at  $192^\circ$ , and begins to sublime in needles. Its aqueous solution reddens litmus.

				Laurent & Gerhardt.
28 C	.....	168	...	69.71
N	.....	14	...	5.81
11 H	.....	11	...	4.56
6 O	.....	48	...	19.92
<hr/>				
$C^{28}NH^{11}O^6$	.....	241	...	100.00

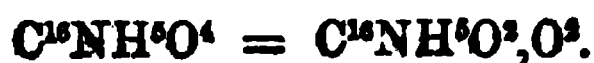
Phenyl-phthalamic acid evolves aniline when partially fused with hydrate of potash.

It dissolves to a very slight extent in cold water, but more freely in hot water.

The acid neutralised with ammonia does not precipitate chloride of barium or chloride of calcium; with acetate of lead and with salts of silver, it forms white precipitates.

It is very soluble in *alcohol* and in *ether*.

### Phthalimide.



LAURENT. (1836.) *Ann. Chim. Phys.* 61, 121; *Rev. scient.* 13, 600; *N. Ann. Chim. Phys.* 23, 119.

#### *Naphthalimide.*

*Formation.* By heating acid phthalate of ammonia:



phthalamate of ammonia. (p. 30.)

\* It will be convenient to treat of the following derivatives of phthalic acid, sooner than is in accordance with the general plan of the work.

**Preparation.** When acid phthalate of ammonia is distilled in a retort, water is set free and phthalimide sublimes.

**Properties.** Colourless. Crystallises from ether by spontaneous evaporation in six-sided prisms, derived from a rhomboidal prism with angles of  $113^\circ$ . Melts when heated, and solidifies in a striated mass on cooling; at a stronger heat, it boils and sublimes in very light flakes. Inodorous and tasteless.

					Laurent.	
16 C	.....	96	...	65.30	.....	64.65
N	.....	14	...	9.52	.....	8.90
5 H	.....	5	...	3.40	.....	3.10
4 O	.....	32	...	21.78	.....	23.35
<hr/>					<hr/>	
$C^6NH^3O^4$	.....	147	...	100.00	.....	100.00

Isomeric with isatine.

**Decompositions.** 1. Phthalimide is not attacked by chlorine or by weak or diluted acids. — 2. It dissolves in strong sulphuric acid when heated; and if water is added to the solution, phthalic acid separates out on cooling. — 3. Boiled with an alcoholic solution of potash, it evolves ammonia and forms phthalate of potash.

**Combinations.** Phthalimide is insoluble in cold water, and but slightly soluble in hot water.

**Silver-phthalimide.** — A boiling alcoholic solution of phthalimide does not precipitate nitrate of silver; but on addition of ammonia, it deposits a pulverulent precipitate or crystalline spangles, which dissolve in hot ammonia and crystallise out unchanged; its solution in ammonia and a little hot water deposits needles, which appear to be phthalamate of ammonia.

					Laurent.	
Ag	.....	108	...	42.52	.....	41.4
$C^6NH^3O^4$	.....	146	...	57.48	.....	
<hr/>					<hr/>	
$C^6NH^3AgO^4$	.....	254	...	100.00	.....	

When heated, it melts, swells up and forms a black mass, which at a higher temperature, assumes a beautiful metallic gold-green colour; phthalimide sublimes at the same time. (Gerhardt, *Tr.* 3, 488.)

Phthalimide dissolves largely in boiling alcohol or ether.

### Phenyl-phthalimide.



LAURENT & GERHARDT. (1848.) *N. Ann. Chim. Phys.* 24, 189.

On melting together phthalic acid and aniline, they solidify on cooling. The substance is pulverised and treated with boiling alcohol, in order to

free it from impurities which colour it. A crystalline powder remains which is purified by sublimation and recrystallisation from boiling alcohol.

It forms beautiful colourless needles. Melts at  $203^{\circ}$ , and begins to sublime in beautiful needles before melting. The fused mass becomes crystalline on solidifying.

						Laurent.	
28 C .....	168	...	75.35	.....	75.3	...	74.8
N .....	14	...	6.27				
9 H .....	9	...	4.04	.....	4.2	...	4.1
4 O .....	32	...	14.34				
<hr/>							
$C^{28}NH^9O^4$ .....	223	...	100.00				

With fused hydrate of potash, it forms aniline and phthalate of potash. It dissolves in boiling ammonia as phenylphthalamic acid. It is insoluble in water.

### Nitrophthalimide.

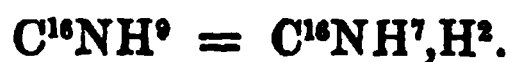


LAURENT. (1850.) *Compt. rend.* 31, 539.

Produced by melting nitrophthalate of ammonia.

*Azo-nucleus*  $C^{16}NH^7$ .

### Phthalidine.



L. DUSART. (1855.) *N. Ann. Chim. Phys.* 45, 335; *Chem. Centr.* 1856, 8.

*Formation.* By the action of sulphuretted hydrogen on nitrophthalin (p. 20), in presence of alcohol and ammonia.

*Preparation.* A mixture of an alcoholic solution of nitrophthalin and sulphide of ammonium is heated to  $50^{\circ}$  for several hours in the water-bath; the greater part of the alcohol is distilled off; the remainder evaporated almost to dryness at a gentle heat; the residue extracted with dilute hydrochloric acid; and the filtrate saturated with potash. The precipitate is at first white and then redissolves in the acid solution with a beautiful blue colour; on adding an excess of potash, flesh-coloured flakes are formed, which gradually become denser and dark. The precipitate is washed on a filter with water, until the filtrate no longer exhibits an alkaline reaction; it then becomes crystalline.

*Properties.* Phthalidine crystallises from its aqueous solution after the lapse of a few days in beautiful needles. When melted and cooled, it forms a crystalline mass of the colour of realgar. It melts at about  $22^\circ$ ; and when it solidifies the thermometer rises to  $34.5^\circ$ . It smells like naphthalin, and tastes unpleasantly pungent. Its solutions do not restore the blue colour to red litmus, but its vapour (at what temperature? L.) turns it immediately blue. Very small quantities of phthalidine impart a beautiful blue colour to solutions of ferric salts.

		At $130^\circ$		Dusart.
16 C .....	96	....	80.67	80.45
N .....	14	....	11.77	11.24
9 H .....	9	....	7.56	7.42
<hr/>				
$C^{16}NH^9$ .....	119	....	100.00	99.11

*Decompositions.* 1. Phthalidine begins to boil at  $255^\circ$ , but the thermometer rises very rapidly, while decomposition takes place, and a carbonaceous residue remains behind. — 2. It is converted into a yellowish-white mass by chlorine water. — 3. It reduces nitrate of silver, while very brilliant crystals are deposited from the solution. The aqueous solution produces a grey precipitate with mercurous salts, and a yellow precipitate with ferrous salts. It blackens on the addition of chloride of gold. A solution of hydrochlorate of phthalidine is rapidly decomposed by bichloride of platinum, assuming a green colour, and depositing blue flakes which blacken on drying; a warm saturated solution of the salt forms with bichloride of platinum, beautiful yellow crystals which partially decompose on drying.

*Combinations.* Phthalidine dissolves pretty readily in cold water. The salts of phthalidine are soluble in water and in alcohol.

*Sulphate of Phthalidine.*  $C^{16}NH^9, HO, SO^3$ . — Sulphuric acid unites directly with phthalidine, and forms a dark green mass which attracts moisture from the air and becomes blue. The crystallised salt is obtained by double decomposition, or by mixing the alcoholic solution of the base with sulphuric acid. It dissolves much less readily in alcohol than the other salts. Contains 23 per cent.  $SO^3$  (calculated 23.80).

*Hydrochlorate of Phthalidine.* — On saturating a warm alcoholic solution of the base with hydrochloric acid, it immediately becomes filled with violet-blue crystals.

				Dusart.
16 C .....	96	....	61.78	60.65
N .....	14	....	9.01	9.47
10 H .....	10	....	6.43	6.64
Cl .....	35.4	....	22.78	
<hr/>				
$C^{16}NH^9, HCl$ ....	155.4	....	100.00	

*Nitrate of Phthalidine.* —  $C^{16}NH^9, HO, NO^3$  is formed by mixing the alcoholic solution of the base with nitric acid. It contains 15.0 per cent. of nitrogen (calculated 15.33).

Phthalidine dissolves in every proportion in warm alcohol or ether.

**Ethyl-phthalidine.**

DUSART. *N. Ann. Chim. Phys.* 45, 335.

Liquid having the odour of phthalidine. It distils without decomposition.

*Hydriodate of Ethyl-phthalidine* form flakes of silvery lustre. It gives off iodine at  $100^\circ$  and becomes yellow.

*Hydrochlorate of Ethyl-phthalidine* is very much like the preceding compound.

				Dusart.
20 C	.....	120	....	65.43
N	.....	14	....	7.63
14 H	.....	14	....	7.63
Cl	.....	35.4	....	19.31
<hr/>				
$\text{C}^{20}\text{NH}^{13}, \text{HCl}$	....	183.4	....	100.00

*Azo-nucleus*  $\text{C}^{16}\text{NH}^5\text{O}^2$ .

**Indigo-blue**  $\text{C}^{16}\text{NH}^5\text{O}^2$ .

- QUATREMÈRE D'ISJONVAL. *Phys. & chem. Abhandl.* Leipz. 1785, 1, 3.  
 BERGMANN. *Opusc.* 5, 1.  
 PLANER (& TROMMSDORFF). *Untersuchung der blauen Farbe im Waidkraute.* Erfurt, 1780.  
 BUCHOLZ. *A. Gehl.* 3, 3.  
 GIOBERT. *Traité sur le Pastel.* Paris, 1813; *J. Phys.* 78, 462.  
 CHEVREUL. *J. Phys.* 65, 309; abstr. *N. Gehl.* 5, 373; *J. Phys.* 66, 369; *Ann. Chim.* 66, 8; 68, 284; abstr. *Schw.* 5, 291; *Gilb.* 41, 345; 42, 315; *A. Tr.* 19, 93.  
 THOMSON. *Thoms. Ann.* 15, 465; *Schw.* 31, 482.  
 DÖBEREINER. *Schw.* 13, 480; 14, 372; *N. Tr.* 1, 2, 443.  
 W. CRUM. *Phil. Ann.* 5, 81; *Schw.* 38, 22.  
 RUNGE. *N. Tr.* 7, 1, 72.  
 LE ROYER & DUMAS. *J. Pharm.* 8, 377; abstr. *Schw.* 36, 277.  
 ROBIQUET. *J. Pharm.* 25, 62.  
 LIEBIG. *Mag. Pharm.* 18, 192; abstr. *Schw.* 51, 60.  
 BERZELIUS. *Pogg.* 10, 105 & 107.  
 HERVY. *J. Pharm.* 26, 290; *Pharm Centr.* 1840, 805.  
 GIRARDIN & PREISSER. *J. Pharm.* 26, 344; *Pharm. Centr.* 1840, 817.  
 WESTON. *Quart. Jour. N. Ser.* 5, 296.

- DUMAS. *Ann. Chim. Phys.* 63, 265; *N. Ann. Chim. Phys.* 2, 204; *J. pr. Chem.* 10, 222; 24, 193; *Pharm. Centr.* 1837, 339; 1841, 596.  
 ERDMANN. *J. pr. Chem.* 19, 321; 24, 3; *Pharm. Centr.* 1841, 705.  
 FRITZSCHE. *J. pr. Chem.* 23, 67; *Ann. Pharm.* 39, 76; *J. pr. Chem.* 28, 193; *Pharm. Centr.* 1843, 4.  
 SCHUNCK. *N. Phil. Mag. J.* 10, 73; *J. pr. Chem.* 66, 321; *Chem. Centr.* 1856, 50. Further. *N. Phil. Mag.* 15, 99; *J. pr. Chem.* 73, 268.

*Indigo, coloured Indigo, oxidised Indigo, Insoluble blue Indigo, Pigmentum Indicum, Indigotine.*

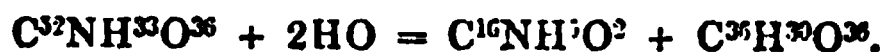
Indigo was used by the ancients in India and Egypt, and is mentioned by Dioscorides and Pliny under the names of *ινδικον* and *indicum*; it first came into use in Europe at the commencement of the 16th century, while woad was already cultivated in France and Germany in the 6th century.

The following plants yield indigo blue; *Indigofera tinctoria*, *anil*, *disperma*, *argentea*, *cerulea*, *pseudotinctoria*, *hirsuta*, *caroliniana*, (Clamor Marquardt did not obtain indigo from *Indigofera australis*), *Isatis tinctoria* and *lusitanica*, *Nerium tinctorium*, s. *Wrightia tinctoria*, *Marsdenia tinctoria*, *Asclepias tingens*, *Polygonum tinctorium* and *chinense*, *Galega tinctoria* (Hayne, *Berl. Jahrb.* 1817, 118), the white parts of the blossom of *Tankervillia cantonensis* (Link) and *Limodorum veratrifolium*. The occurrence of indigo in *Wrightia tinctoria*, *Marsdenia tinctoria*, and *Asclepias tingens* is doubted by Clamor Marquardt (*Repert.* 57, 15). The following plants yield a blue colouring matter similar to indigo. *Mercurialis perennis*, *Melampyrum arvense* and *cristatum*, *Polygonum fagopyrum*, (Clamor Marquardt), and *Polygala bracteolata*. (Dierbach, *Ann. Pharm.* 3, 45), *Croton tinctorium* and *verbascifolium*, *Phytolacca decandra* and *mexicana* (Landerer, *Repert.* 84, 69), *Monotropa hypopitys*. (Reinsch, *Jahrb.* 25, 293.)

Indigo-blue is somewhat frequently deposited by unhealthy urine, especially in tuberculosis. (Hill, *Hassal Chem. Gaz.* 1854, 320; *Ann. Pharm.* 90, 120.)—*Cyanurine* (q. v.), first investigated by Braconnot, reacts differently from indigo-blue.

*Views respecting the nature of the substance in indigo plants, which yields indigo-blue.*—Indigo plants contain only the base of the colouring matter, which of itself is green; it is kept in solution by the carbonic acid evolved in the preparation of indigo; it is set free by the addition of alkalis and absorbs from the air a substance which converts it into indigo-blue. (Roxburgh, *Transact. of the Society of Arts*, vol. 28.) *Isatis tinctoria* and *indigofera anil* contain a hydrogen-compound of indigo-blue, namely, white indigo (Döbereiner's *woadic acid*), which is held in solution by the sap and when exposed to the air is oxidised to indigo-blue. (Chevreul, Girardin & Preisser.) The indigo-plants contain colourless *indigogen*, which is soluble in water and contains more carbon than indigo-blue, into which it is converted, with formation of carbonic acid, by absorbing oxygen from the air. This oxidation is promoted by heat or by the presence of alkalis, especially by lime; it is arrested by acids, even by carbonic acid. (Giobert.) The leaves of *Polygonum tinctorium* contain a colourless combination of indigo-blue with a resin which may be extracted by ether and is soluble in water; the resin is decomposed by acids or alkalis. (Hervy.) According to Schunck, no plant can contain

white indigo, since the latter requires free alkali for its solution, while the sap of plants is always acid and moreover contains free oxygen. Woad contains a compound called *indican*,  $C^{12}NH^{13}O^{16}$ , which is readily soluble in water; this substance when boiled with strong acids, splits up into blue indigo and a peculiar kind of sugar, without the intervention of oxygen :



*Formation.* By the action of oxygen upon white indigo :



By boiling *indican* with strong acids. (Schunck.)

*Preparation of Commercial Indigo.* 1. *From Fresh Leaves.* — In Bengal, the plants, which are cut close to the ground whilst the blossom is unfolding, are placed in a brick cistern—(*steeping vat*, *Gährungsküpe*, *trempoire*, *pourriture*), which is filled several inches deep with cold water, and allowed to ferment. At 30° the fermentation is finished in 12 or 15 hours; at lower temperatures it requires a longer time. The gas evolved is a mixture of carbonic acid and atmospheric air from which the oxygen has been absorbed; it was found to contain at first 27·5 per cent. carbonic acid, 5·8 per cent. oxygen, and 66·7 per cent. nitrogen; at a later stage, 40·5 per cent. carbonic acid, 4·5 per cent. oxygen and 55·0 per cent. nitrogen; when the fermentation was over, the solution evolved on boiling, a gas which contained 78·0 per cent. carbonic acid, 2·3 per cent. oxygen and 19·7 per cent. nitrogen. A second experiment gave 86 per cent. carbonic acid, and very little oxygen. The leaves lose from 12 to 14 per cent. of solid matter during the fermentation, but appear still fresh and green after it is over. When the liquid no longer rises, it is drawn off into the *beating vat* (*Schlageküpe*, *batterie*) which stands lower, where it is kept stirring for an hour and a half or two hours, whereupon carbonic acid is evolved and the indigo at first separates in large flakes. When, after being repeatedly stirred, it forms grains like fine sand and the solution is clear, the indigo is allowed to settle. After 2 or 3 hours the liquid is drawn off from the deposit. (If the fermentation is properly conducted, the indigo settles readily down, the liquid is of a malaga-brown colour, and forms a thick foam which rapidly disappears.) — For further particulars see *J. Pharm.* 26, 276. The deposit is boiled for 3 or 4 hours in a copper vessel and then thrown upon a linen filter; it is afterwards pressed, cut into squares and dried by heat. 1000 pts. of the solution of the leaves yield from 0·5 to 0·7 pts. of indigo; more is precipitated on the addition of potash-ley or lime-water, but it is not so pure.

Respecting the manufacture of indigo in the Caucasus, see *Dingl. pol. J.* 126, 304.

2. *From dry leaves.* — *a.* In the southern part of India, the ripe leaves which have been completely dried by the sun, are kept for 4 weeks, when they assume a leaden-grey colour (if kept for a longer time they become black and yield less indigo). The leaves are then covered with six times their bulk of cold water, and after two hours the green solution is drawn off into the beating vat; it is kept stirring (for about 2 hours) till it becomes dark blue and the indigo begins to precipitate then mixed with lime-water, allowed to settle down and treated as in the preceding method. — Indigo is obtained in the same way in the south of France from a hot extract of *Nerium tinctorium* and *Polygonum tinctorium*. (Compare *J. Pharm.* 26, 276; *J. pr. Chem.* 16, 180.) Indigo was formerly



prepared from woad in a similar manner, by employing tepid water and precipitating with lime-water; a deeper colour was imparted to the product by extracting the carbonate of lime with hydrochloric acid. The preparation of indigo from *Polygonum tinctorium* is rendered difficult by a resin which the plant contains. This resin is separated by mixing the bruised leaves with one-tenth of their weight of protosulphate of iron, and adding a sufficient quantity of water together with excess of carbonate of potash; the whole is then thrown upon a filter, and the solution mixed with sufficient nitric acid to render it slightly acid. On neutralising with carbonate of potash, it becomes blue and deposits all the indigo within 24 hours; the indigo has now the same properties as that obtained from *Indigofera*. Gaudry, (*N. J. Pharm.* 5, 133.)

Commercial indigo contains from 50 to 90 per cent. of indigo-blue; the remainder consists of indigo-red, indigo-brown, indigo-gluten, carbonate of lime, magnesia, alumina and oxide of iron. — Compare Ure, (*N. Quart. J. of Sc.* 7, 160; also *Dictionary of Chemistry*, 4th Ed. p. 529.) Schlumberger (*J. pr. Chem.* 26, 217). — (See further *the Valuation of Indigo*, p. 59).

*Purification of Commercial Indigo.* a. *By extracting the impurities.* — Powdered indigo is boiled with water, then with alcohol, then with hydrochloric acid and again with water. (Chevreul.) It is boiled with hydrochloric acid, then with strong potash, and then repeatedly with alcohol. (Berzelius.) — Fritzsche removes the indigo-red by boiling with an alcoholic solution of potash. (*J. pr. Chem.* 28, 199.)

b. *By oxidising the Indigo-white contained in the vat with air.* 1. *Cold vat.* a. *Blue vat (Vitriolküpe, Cuve à la couperose).* — 1 pt. of finely ground indigo is mixed with hot water, in which 4 pts. of quick lime are slaked; and to this is added a solution of 3 pts. of sulphate of iron free from copper, the whole being stirred. (If the sulphate of iron is yellowish, one-third more is taken.) Water is then added to the amount of 100 or 200 times the weight of the sulphate of iron, according as the dye is required dark or light, and the whole, after being stirred, is allowed to rest. The proportions quoted are those most commonly employed in dyeing; when the indigo is particularly pure, more lime and sulphate of iron must be taken. An excess of lime yields a *sharp vat (scharfe Küpe)*, from which the threads of the stuff do not readily take up the dye; too little lime yields a *soft vat (leise Küpe)*, which does not dye so well. On the addition of carbonate of potash, a compound of indigo-white with potash is formed. A sediment is formed and a yellow solution, which becomes covered with a copper-coloured film (flower); the solution is drawn off from the sediment, and deposits tolerably pure indigo-blue on exposure to the air. — Thomson digests commercial indigo with lime, sulphate of iron and water, and exposes to the air the decanted solution of the compound of indigo-white with lime; he then removes the carbonate of lime from the blue precipitate with hydrochloric acid, and the indigo-red with water, afterwards washes with water and dries. — Berzelius mixes 3 pts. of indigo (purified according to 1) with 6 parts of quick lime freshly slaked, 4 pts. of sulphate of iron, and 450 pts. of boiling water; he then closes the vessel and shakes repeatedly; allows the whole to subside and removes the yellow solution by means of a syphon; again adds hot water and draws it off after repeated shaking; mixes the whole of the solution with hydrochloric acid; exposes it to the air and agitates it till the indigo is completely oxidised; then throws it on a filter and washes with water.

— Erdmann mixes together 1 pt. of indigo, 2 pts. of sulphate of iron, 3 pts. of lime and 60 pts. of water; draws off the clear solution and mixes it, with repeated stirring, with dilute hydrochloric acid; and washes the precipitate in contact with the air. The residue yields fresh quantities of indigo-blue when again stirred up with hot water, and with lime if necessary. — The indigo-blue thus obtained contains a little gypsum, at most 0.75 per cent., and indigo-red, which it is difficult to remove by boiling with alcohol; it is better to reduce the indigo again in the cold vat and precipitate it with hydrochloric acid. — According to Dumas, a little sulphide of calcium is formed in the vat, and hence sulphur is mixed with the indigo when it is precipitated by hydrochloric acid; this he removes with bisulphide of carbon. — In the so-called *orpiment-vat*, a solution of the compound of indigo-white with potash is formed in a mixture of indigo-blue with tersulphide of arsenic, potash and water by the oxidation of the resulting sulpharsenite of potassium; the solution deposits indigo-blue when exposed to the air.

Protochloride of tin may be used in the indigo-vat (p. 45).

*β. Warm vats.* — 1. *Woad-vat.* (*Pastel-vat.*) On mixing from 2 to 6 pts. of finely powdered indigo with from 30 to 50 pts. of woad, 2 pts. of madder, 2 pts. of bran, 1 to 8 pts. of potashes and  $\frac{1}{2}$  pt. of lime, and warming with 1000 pts. of water (6000 to 7000 litres) at 80°, a fermentation is set up in which water is decomposed and the nascent hydrogen forms indigo-white, which combines with the ammonia simultaneously formed. The brownish yellow liquid first becomes green on exposure to the air, and then deposits indigo-blue; it may be used for dyeing for three to six months if it be kept warm, and madder, bran, indigo or potashes added from time to time. (Instead of madder, beetroot-molasses and malt may be advantageously used). — 2. In the *potash* or *Indian vat*, in which woad and lime are not used, 3 pts. of indigo are added to a mixture of 2 pts. of madder, 2 pts. of wheat-bran, 6 pts. of potashes and 1000 pts. of water at 60°; after 36 hours, 3 pts. of potashes, and after 12 hours more the same quantity of potashes, are likewise added. (This vat is easier to manage than the woad vat.)

*γ.* To obtain indigo-blue in the crystalline state, 4 oz. of raw indigo and 4 oz. of grape-sugar are introduced into a flask capable of containing 12 lbs. water, to which 6 oz. of the strongest soda-ley are added; the whole is well shaken; and the flask completely filled with hot alcohol. It is then tightly corked and left for several hours, until the solution is sufficiently clear to permit its being siphoned off into a larger flask, in which it is allowed to stand loosely covered. The solution, at first of a beautiful yellowish red colour, now gradually turns blue, whilst indigo separates out. The solution is filtered and the indigo is washed, first with alcohol and then with water, till the filtrate is colourless. In this manner 2 oz (50 per cent.) of pure indigo-blue are obtained. If the brown alcoholic solution is poured back hot into the first flask, it yields 3 per cent. more indigo; but it is then nearly exhausted. (Fritzsche, Marchand.) — Indigo also forms a vat immediately with grape-sugar, caustic, soda, and hot water; the decanted solution, when exposed to the air, deposits indigo containing a quantity of indigo-red, which may be extracted by an alcoholic solution of soda. (Fritzsche.)

*c. By sublimation.* When powdered commercial indigo is heated on a watch-glass, a silver dish, or a spoon, a network of crystals is formed,

which may be removed with a pair of forceps, and the crystals carefully separated from adhering particles of carbon, under a magnifying glass. (Le Royer & Dumas; Dumas.) Chevreul sublimed indigo in a crucible fitted with a cover over a hot fire; much indigo was decomposed in this operation. — Crum heats indigo between two platinum crucible lids, which are separated from one another by a distance not greater than  $\frac{3}{8}$  inch, till the hissing sound ceases. — Berzelius sublimes indigo in an exhausted retort, of the size of a chicken's egg, cuts off the upper part of the retort when the crystals have sublimed, and separates the lower crystals from the adhering particles of carbon. The crystals are freed by ether from traces of oil and resin. — Taylor stirs up an intimate mixture of 2 pts. finely powdered indigo and 1 pt. gypsum with water into a thin paste, which he spreads upon sheet-iron in layers 2 inches broad and  $\frac{1}{8}$  inch deep. These are dried by exposure to the air, then heated at one end with a spirit-lamp till red vapours are evolved, and so the operation is continued. If the mass catches fire, it is extinguished by a drop or two of water. The velvety indigo is easily separated, and may be purified by alcohol and ether. (*Med. Gaz.* 1843, 130.)

*Preparation of Indigo-blue from Indican.* — According to Schunck, the aqueous solution of indican from woad-leaves, which must not be too dilute, is boiled with sulphuric or hydrochloric acid; and the abundant purple-blue precipitate is filtered off and washed, first with water and then with boiling alcohol, till the filtrate is of a pure blue colour: the residue is said to consist of pure indigo-blue. — According to Schunck's latest experiments, it appears that nitric, oxalic, tartaric, and acetic acid are also capable of converting indican into blue indigo: acetic acid, however, acts less powerfully than the rest.

*Properties.* Indigo-blue sublimes in right rhombic prisms (Fig. 75;  $u : u = 103^\circ 30'$ ,  $u : m = 128^\circ 15'$ ,  $u : n = 149^\circ 12'$ ;  $n : n = 165^\circ 6'$ ,  $y : y = 108^\circ$ ,  $y : m = 126^\circ$  (Miller, *Pogg.* 23, 559); in six-sided prisms, the bases of which are replaced by two faces which seem to form an obtuse angle with one another (derivable from a rhombic prism with angles of  $32^\circ$  and  $148^\circ$ .) (Laurent.) Its lustre is semi-metallic, and by reflected light, dark red inclining to copper-red (according to Crum, it is red when viewed obliquely under the microscope; and of a brilliant blue when viewed perpendicularly). When prepared in the wet way, it is dark blue, and acquires by pressure a dark copper colour and almost metallic lustre. It is inodorous and tasteless, and does not react upon vegetable colours. — In open vessels, it volatilises at about  $288^\circ$  in dark purple-red vapours; in closed vessels, it decomposes partially when heated. (Crum.) — It volatilises without decomposition only in a current of air or in vacuo; the powder dropped on a piece of heated platinum foil, volatilises in purple vapours without leaving a residue, each particle being supported by the vapour without coming in contact with the foil. (Dumas.)

			Crum.	Ure.	Le Royer & Dumas.		
					a.	b.	c.
16 C.....	96 ...	73.28 ...	73.22 ...	71.37 ...	71.71 ...	74.81 ...	73.26
N.....	14 ...	10.68 ...	11.26 ...	10.00 ...	13.45 ...	13.98 ...	13.81
5 H .....	5 ...	3.82 ...	2.92 ...	4.38 ...	2.66 ...	3.33 ...	2.50
2 O.....	16 ...	12.22 ...	12.60 ...	14.25 ...	12.18 ...	7.88 ...	10.43
$C^{16}NH^5O^2$ ...	131 ...	100.00 ...	100.00 ...	100.00 ...	100.00 ...	100.00 ...	100.00

Dumas.				Erdmann.		Laurent.	
<i>a.</i>		<i>b.</i>	<i>c.</i>				
72.9	....	72.91	....	73.12	....	73.99	.... 73.23
10.3	....	10.80	....	....	10.61		
4.0	....	4.08	....	....	3.80	....	3.89
12.8	....	12.21					
<hr/>				<hr/>			
100.0	....	100.00					

The indigo-blue analysed by Crum, by Le Royer & Dumas (*c*), by Dumas (*a*), and by Erdmann and Laurent, was obtained by sublimation; that analysed by Ure contained indigo-red; *a*, analysed by Le Royer & Dumas, was obtained by boiling (p. 38, *a*); *b*, from the blue vat (p. 38, *b*). Erdmann & Marchand found previously, 75.7 per cent. carbon, in sublimed indigo-blue, exhausted by boiling with alcohol (*J. pr. Chem.* 19, 321).

Indigo-blue is isomeric with cyanide of benzoyl.

*Decompositions.* 1. Indigo-blue melts and boils when heated in contact with the air; at higher temperatures, it burns with a bright and very smoky flame, leaving a residue of difficultly combustible charcoal. (Berzelius.) — By exposure to air containing ozone it is quickly converted into isatin. (Erdmann, *J. pr. Chem.* lxxi. 209.) — 2. By dry distillation it yields a very little undecomposed sublimate, together with carbonate and cyanide of ammonium, aniline, empyreumatic oil, and a large residue of shining charcoal. 11 pts. of indigo-blue yield, in this operation, 1.88 pts. of sublimed indigo and 6.44 pts. of charcoal; if the heat be continued till the sublimed indigo is completely destroyed, there are formed, amongst other products of decomposition, 0.19 nitrogen, 0.28 carbonic acid, 0.8 carbonic oxide and hydrocarbons, and 0.8 ammoniacal water. (Crum.) On heating indigo-blue in vacuo, a brown oil is formed together with a large proportion of sublimed indigo, but no permanent gas or aqueous liquid; by rapid heating, more sublimate is obtained, and a fused shining charcoal; on heating more gradually, less sublimate is formed, together with a dull earthy charcoal. (Berzelius. — compare Unverdorben, *Pogg.* 8, 397.) — 3. Dry chlorine does not act upon indigo-blue between 0° and 100°. If indigo-blue is stirred up with water into a thin paste, and chlorine passed through, while the whole is kept cool, the mass becomes first greyish-green and then yellow. Neither carbonic acid nor any other gas is evolved. An orange-coloured deposit is formed, and a yellowish-red solution; on distilling, terchlorocarboic acid and terchloraniline sublime, and a liquid distils over which smells of anisic acid, and contains hydrochloric acid and terchlorocarboic acid. The residue in the retort dissolves in boiling water, leaving a brown resin, which is formed in small quantity only, if the mass is cooled as much as possible during the action of the chlorine, and the passage of the chlorine is interrupted before all the indigo-blue is destroyed. The boiling aqueous solution deposits, on cooling, a yellowish-red crystalline powder, which yields chlorisatin and bichlorisatin when recrystallised from alcohol. (Erdmann.) Berzelius took advantage of the destruction of indigo-blue by chlorine to determine the amount of indigo-blue contained in commercial indigo. To a known quantity of chlorine water he added pure finely-powdered indigo as long as it dissolved with yellow colour, and then ascertained how much of the indigo to be tested was decolorised in the same way by the same quantity of chlorine water; the amount of commercial indigo employed contained the quantity of indigo-

blue which was used in the first experiment. — This method is inaccurate, since undissolved indigo produces no perceptible difference in the colour of the solution, and requires more decolorising matter than is present in the solution; the indigo to be tested must, therefore, always be completely dissolved. (Mohr, *Lehrb. der Titrir-methoden*, 191.) (For tests for indigo see *Sulphindigotic Acid*, p. 59.) — 4. *Bromine* acts upon indigo in the same manner as chlorine. On treating moist indigo with bromine, a yellow mass is formed, which yields, by distillation, terbromocarbolic acid and terbromaniline; the residue contains a little bromisatin, a large proportion of bibromisatin, and a little resinous matter. (Erdmann.) — 5. *Iodine* decomposes indigo only when heated. (Berzelius.) — 6. Indigo is decomposed by heating it with chlorate of potash and hydrochloric acid. Only traces of chloranil are formed. (Hofmann.) — 7. When boiled with dilute *nitric acid*, it gives off a large quantity of gas, and forms isatin and a brown resin; with a stronger acid it forms principally nitrosalicylic acid (xii, 305), and with an excess of nitric acid of sp. gr. 1.43 it yields picric acid (xi, 212); at the same time carbonic acid, prussic acid, oxalic acid, and the so-called artificial indigo-resin are formed. — 5 pts. of fuming nitric acid become so violently heated with 1 pt. powdered commercial indigo that the mass takes fire. (Woulfe, Winckler, *Repert.* 41, 330.) — When indigo is boiled in a retort with nitric acid and the receiver surrounded with ice, yellow needles pass over. These when heated, melt into a clear yellow oil, and distil without decomposition at a higher temperature; they have an aromatic odour and a sweet aromatic taste. They redden litmus, and dissolve very abundantly in water with yellow colour; they dissolve in ammonia, without yielding a crystalline product on evaporation. They form, with potash, a solution which is at first dark yellow, and soon becomes filled with microscopic crystals. The crystals are readily soluble in water, from which they crystallise unchanged on evaporation; they appear of an orange colour by reflected light, and bluish green by transmitted light. (Fritzsche.) — A solution of sulphate of nitric oxide in oil of vitriol forms with indigo in the cold a green solution which when heated becomes of a beautiful rose colour, and then dark purple red. (Prevostaye, *Ann. Chim. Phys.* 73, 377.) — 8. Concentrated *chromic acid* destroys indigo-blue immediately, especially when heat is applied, with violent evolution of carbonic acid and precipitation of sesquioxide of chromium. Dilute chromic acid forms a clear yellow-brown solution with indigo; if this is heated to near the boiling point and filtered, isatine crystallises out on cooling. (Erdmann.) Chlorochromic acid does not act upon indigo-blue. (Thomson, *Pogg.* 31, 607.) — 9. On boiling indigo-blue with *peroxide of lead*, a pale yellow solution is formed, which becomes turbid on cooling, and leaves a yellow powder when evaporated to dryness. This substance suspended in water and decomposed with sulphuretted hydrogen, yields a brownish-yellow filtrate, which on evaporation leaves a residue consisting of a small quantity of brown resin and a few crystals. The sulphide of lead contains a brown resin, melting at  $100^{\circ}$ , which may be extracted by boiling alcohol, and precipitated by water; boiling water extracts from it a substance which on evaporation, deposits crystals mixed with resin. (Erdmann.) — 10. *Manganic sulphate*, *manganate*, of *potash* and *permanganate of potash* decolorise indigo. (Lefort, *Rev. scient.* 16, 358.) On heating indigo-blue for a considerable time with aqueous *osmic acid*, oxalic acid is formed. (Buttlerow, *J. pr. Chem.* 56, 278.) —



11. When the vapour of anhydrous sulphuric acid is passed over roughly pulverised commercial indigo, the latter swells up, becomes heated, and a beautiful purple-red liquid is formed, which is transparent in thin layers, and solidifies into a crimson mass. In contact with the air, it evolves sulphurous acid (probably on account of the impurities of the indigo), and dissolves in common sulphuric acid with a violet colour; on dissolving it in water, charcoal separates out and a dark blue solution is formed. (Döbereiner, Bucholtz, Bussy.) Indigo dissolves with evolution of heat in excess of fuming or in common *sulphuric acid* (no gas is evolved if the indigo is pure) with formation of sulphindigotic acid; if an excess of sulphuric acid is not added, more or less sulphophœnicic acid is formed. According to Berzelius, hyposulphindigotic acid is also formed when indigo is dissolved in fuming sulphuric acid. — Indigo-blue dissolves in cold sulphuric acid, first with a yellow colour, which afterwards becomes green, and finally of a beautiful blue. (Housmann, *Journ. de Phys.* 1788, March, Chevreul.) From the solution while still yellow, undecomposed indigo-blue may be precipitated by water; the yellow colour changes to blue in a few hours in a closed vessel, since sulphophœnicic acid is formed, which is gradually converted into sulphindigotic acid. The solution of indigo is attended with evolution of heat; no sulphurous acid is formed if pure indigo is employed, even if the solution is kept at 100° for a considerable time. The quantity of fuming sulphuric acid required for solution is less the more anhydrous acid it contains; 1½ times as much of the strongest common sulphuric acid is required as of the fuming acid. The solution is much more complete when effected at 100°. (Crum, *comp.* Bucholtz.) When indigo is more strongly heated with sulphuric acid, sulphurous acid is evolved, and a brown oily liquid formed. (Döbereiner.) Liquid anhydrous sulphurous acid does not act upon indigo. (Bussy.) Anhydrous phosphoric acid and hydrated phosphoric acid are without action upon indigo; also concentrated hydrochloric acid. (Döbereiner.)

12. Indigo-blue is but slightly attacked by prolonged boiling with dilute *potash*; when the boiling point has reached 100°, the indigo is completely decomposed, whilst no gas is given off, and only traces of ammonia and aniline are evolved with the aqueous vapour. (Fritzsche.) According to Gerhardt (*Rev. scient.* 10, 371), indigo-white and isatate of potash are formed in this reaction:



According to Fritzsche, a yellowish-red solution is first formed, on which a dark coloured substance floats, and from which yellow crystals of chrysanilate of potash are separated by continued boiling; on cooling, it solidifies into a crystalline mass, consisting principally of chrysanilate of potash. The dark-coloured substance is most abundantly formed when the indigo is made into a thin paste with water and boiled, and then treated with hydrate of potash; it is formed in much smaller quantity when powdered indigo is gradually added to a potash-ley boiling at 150°. — The crystalline mass, when water is poured over it, immediately yields indigo-blue (in the same state as from the indigo vat); the filtered solution also continues to deposit indigo-blue when exposed to the air. If the crystalline mass is immediately incompletely neutralised with an acid, a bluish-green precipitate is formed, and the solution contains chrysanilate of potash (xii, 329). If the crystalline mass is treated with alcohol instead of water, a dark green solution is obtained, which,

if the dark coloured substance was formed in large quantity, absorbs oxygen, and deposits indigo-blue in thin four-sided laminæ; chrysanic acid separates out from the dark green filtrate on addition of a dilute acid. If long exposed to the air, the filtrate becomes yellowish-brown, the chrysanic acid being converted into anthranilic acid. When potash-ley boiling at  $150^\circ$ , is saturated with chlorate of potash and indigo-blue is added, the latter dissolves with dark orange-red colour. The whole solidifies on cooling, and when dissolved in water deposits only a little indigo-blue and then yields chrysanic acid free from chlorine. (Fritzsche.) On melting indigo with potash, anthranilic acid is formed, with evolution of hydrogen. According to Gerhardt, isatic acid is first formed, which yields anthranilic acid on the further action of potash.



By heating indigo-blue with hydrate of potash to  $300^\circ$  (compare xii, 246), Cahours obtained salicylic acid, resulting from the decomposition of the previously-formed anthranilic acid:



On distilling indigo-blue with hydrate of potash, aniline is evolved:



(Fritzsche); according to Gerhardt, the aniline results from the further action of the potash upon the previously-formed anthranilic acid.



By melting commercial indigo with hydrate of potash, Gerhardt (*Compt. rend.* 13, 309) and Erdmann (*J. pr. Chem.* 27, 250) obtained valerianic acid; Winkler, *Repert.* 78, 70) and Muspratt (*Ann. Pharm.* 51, 271) obtained acetic acid, which was owing to the impurities of the indigo. Compare Liebig (*Ann. Pharm.* 40, 314); Gerhardt (*N. J. Pharm.* 9, 319).

13. Indigo-blue placed in contact with water, an *alkali*, and a *deoxydising substance*, becomes at first coloured green, and is then converted into indigo-white, which forms a yellow solution with alkalis. In this reaction, water is decomposed, the hydrogen being used in the formation of indigo-white, *e. g.*



The following substances react in a similar manner: phosphorus, phosphorous acid, sulphurous acid, hydrosulphuric acid, potassium-amalgam, sulphide of potassium, sulphide of sodium, sulphide of arsenic, sulphide of antimony, zinc, tin, iron, protoxide of iron, protoxide of tin, protoxide of manganese, grape-sugar, and substances undergoing fermentation or putrefaction, as sugar, gluten, urine, woad, madder. Warm putrid urine dissolves indigo-blue, the ammonia-compound of indigo-white being formed. — According to Löwenthal, on the contrary (*J. pr. Chem.* 70, 463), this reduction of blue to white indigo is not produced by salts of sulphurous or phosphorous acid, by sulphide of potassium, sulphide of calcium, manganous salts, or arsenite of soda; but indigo-blue dissolved in sulphuric acid is reduced to indigo-white when mixed with excess of bicarbonate of potash or soda, and then treated with sulphuretted hydrogen. Löwenthal is of opinion that indigo-white is not indigo-blue *plus* hydrogen, but indigo-blue *minus* oxygen.

Formic acid appears to be produced in the action of grape-sugar and potash on indigo-blue. — If the indigo-blue obtained from Fritzsche's sugar vat (p. 39) is filtered off, the brownish green alkaline solution forms, with acids, a brownish green precipitate, which, when washed with water and dried, dissolves for the most part in alcohol with reddish brown colour. The acid filtrate deposits, on evaporation, a brown resinous body, which dissolves slightly in water and completely in alcohol. The brownish-green alkaline solution gives a bluish-green precipitate with lime-water (lime-compound of indigo-brown ?); acids precipitate greenish flakes from the filtrate, and if these are filtered off, the acid solution deposits a brown resin on evaporation. (Fritzsche.)

Urine passed from 12 to 24 hours after 6 grm. of indigo had been swallowed, was of a greenish-violet colour. After several days, a small blue ring had formed on the surface, which in 4 weeks became from  $\frac{1}{4}$  to  $\frac{1}{2}$  of an inch broad, and consisted partly of precipitated indigo, partly of blue-coloured phosphate of magnesia and ammonia. (Starke, *J. pr. Chem.* 56, 13.) The passage of indigo into the urine is mentioned by Pereira (*Art of Healing*, 2, 651), and Roth (*Dissert. Inaug. de Indico*, Berlin, 1834); Kletznisky (*Wien. medicin. Wochenschr.* 1851, 34) opposes this statement.

*Combinations.* Indigo-blue is insoluble in water.

Hot *alcohol* dissolves small quantities of indigo-blue which impart to it a beautiful blue colour; on cooling, the indigo separates out almost completely. Indigo-blue remains dissolved in cold alcohol, only when the alcohol contains indigo-red in solution at the same time. (Chevreul.)

Chloride of ethyl is but slightly coloured by standing over indigo, a portion of which converts it into a beautiful blue liquid, without mixing with the latter; the unchanged portion of the indigo shows a stronger copper-colour than before. (Boullay.) — Sublimed indigo does not dissolve in cold *carbolic acid* (or creosote), but pretty readily when it is hot; the solution forms a blue liquid when mixed with a little alcohol, but the indigo is precipitated by a large quantity of alcohol (Runge, Reichenbach; *comp. Müller, N. Br. Arch.* 15, 92.)

Sublimed indigo dissolves to a small extent in boiling *oil of turpentine* with purple-red colour, but immediately separates out again on cooling. (Crum.)

*Fatty Oils* dissolve indigo-blue only at temperature exceeding 100°, with dark violet colour; the indigo separates out unchanged on cooling; at a higher temperature the indigo is decomposed (*comp. Weston, Br. Arch.* 36, 371).

### *Appendix to Indigo-blue.*

#### 1. Indigo-red.

Indigo-red was first noticed by Chevreul, and was more particularly investigated by Berzelius. (*Lehrb.* 3, 689.) — It is found in commercial indigo, and also accompanies the indigo from *Polygonum tinctorium*. (Hervy.)



*a. From commercial indigo.*—Powdered or commercial indigo is first exhausted with hydrochloric or sulphuric acid, then with a concentrated solution of potash, afterwards washed with water and boiled with alcohol of sp. gr. 0.83 until the solution is no longer coloured red, but bright blue. The dark red alcoholic extract is distilled until most of the alcohol has passed over, and the remainder of the solution is filtered from the indigo-red, which is precipitated in the form of a dark brown powder. The remainder of the indigo-red is separated from the filtrate,—in which it remains together with indigo-blue, in combination with potash,—by evaporating the alcohol, dissolving the residue in water, and precipitating with a slight excess of acetic acid, the indigo-brown remaining in solution, and lastly the precipitated indigo-red is washed with water and dissolved in alcohol, from which it separates on evaporation.

Indigo-red forms a blackish-brown powder or a shining blackish-brown *varnish*.

When heated in *vacuo*, it first yields a colourless sublimate, without evolving any permanent gas, then melts, boils and chars, while colourless crystalline indigo-red sublimes. In the uppermost part of the vessel, the latter resembles fused colourless drops; in the middle part it is brown; and near the heated portion it appears melted, reddish yellow and transparent.—Indigo-red quickly heated in contact with the air, melts, fumes, and burns with a bright smoky flame.—In chlorine-water it becomes yellow and plastic like wax; but on exposure to the air, recovers its hardness and regains its former colour almost completely. (Berzelius.) By chlorine in presence of water it is converted into a brown resin, which is insoluble in water, but soluble in alcohol. (Erdmann, *J. pr. Chem.* 19, 329.)—It dissolves in fuming nitric acid with a beautiful purple colour, which, owing to decomposition, soon passes into yellow. Water precipitates indigo-red, apparently unchanged, from the red solution; from the yellow solution it precipitates yellow flakes like those obtained in the same manner from a solution of indigo-brown in nitric acid.—The red solution of indigo-red in alcoholic soda turns brown on exposure to the air, and deposits, when evaporated, a substance which forms with water a brown solution, depositing brown flakes on the addition of acids. (Fritzsche, *J. pr. Chem.* 28, 196.)

Indigo-red does not dissolve in water, in dilute acids, or even in heated concentrated solutions of the alkalis.—It forms with sulphuric acid a dark-yellow solution, which becomes yellowish red on dilution with water, but without forming a precipitate. The solution is decolorised by steeping silk or wool in it for several hours; while the fabric is dyed yellowish brown or red. It dissolves slightly in alcohol, but more abundantly in ether; the bright-red solutions deposit the indigo-red on evaporation as a dark-red powder. (Berzelius.) It dissolves in cold creosote. (Reichenbach.)

*b. From the leaves of Polygonum tinctorium.*—The fresh leaves are exhausted with ether in a digesting funnel, and after a part of the ether has been distilled off, crystals of indigo-blue separate out, and the remaining solution is evaporated to dryness. The residue is exhausted with alcohol, the solution filtered from a slight brown residue, and again evaporated to dryness; and the residue is purified by hot water, which extracts a little yellow colouring matter.

Indigo-red thus prepared is a beautiful red, resin-like substance; hard, brittle and easily pulverized. Burnt with oxide of copper, it yields carbonic acid and nitrogen in the proportion of 16 : 1. Heated in contact with the air, it softens, melts, swells up, and burns with flame, leaving a bulky mass of charcoal which burns without residue. When heated in a tube, it gives off ammoniacal vapours. Distilled in vacuo, it yields merely ammoniacal oil, and without any crystalline sublimate (probably because too little was employed). — When boiled with nitric acid, it evolves abundant red fumes and dissolves with yellowish red colour, while a waxy substance rises to the surface; on evaporating the solution, it leaves a residue, from which water extracts picric acid, while the so-called commercial indigo-resin remains behind. — It dissolves in sulphuric acid, imparting to it a yellow colour; becomes dark red when acted upon by anhydrous sulphuric acid, and retains this colour on the addition of water. Concentrated hydrochloric acid turns it black but does not dissolve it.

Indigo-red is insoluble in *water*, slightly soluble in *potash* and *ammonia*. The alcoholic solution turns red on addition of baryta-water, lime-water, sub-acetate of lead, or nitrate of silver, and, dark red with protochloride of tin. With solution of alum it forms a beautiful red lake, which is not acted upon by alkaline carbonates.

It is very slightly soluble in *acetic acid*, but dissolves very readily in *alcohol* and in *ether*; the alcoholic solution is precipitated by sulphuric acid. (Hervy, *J. Pharm.* 26, 293; *Pharm. Centr.* 1840, 807.)

The indigo obtained from the flowers of *Tankervillia cantonensis* colours alcohol of 35 per cent. first green, then violet; and the solution yields on evaporation a residue consisting of two substances, the one green and insoluble in alcohol of 45 per cent. (probably chlorophyll), the other of a beautiful red colour, soluble in alcohol, but insoluble in water and ether. This latter substance forms with sulphuric acid, a brown solution from which it is precipitated unchanged by water. (Clamor Marquardt, *Repert.* 7, 1.)

The purple-red solution which is obtained when the purple-blue flakes arising from the decomposition of indican by acids are boiled with alcohol, yields a brown residue of *indirubin* very similar to indigo-red. This substance is insoluble in alkalis, and when heated in a tube, gives off purple vapours and yields a crystalline sublimate. (Schunck, *N. Phil. Mag. J.* 10, 85.)

## 2. Colourless Indigo-red.

### BERZELIUS.

The sublimate obtained by heating indigo-red in vacuo is separated from indigo-red by digesting it with alcohol, in which the latter is more soluble, and is then purified by re-subliming in vacuo.

It crystallises when sublimed, in brilliant, colourless, transparent very fine needles; it crystallises on evaporation from its alcoholic or ethereal solution in transparent colourless grains. It is inodorous, tasteless and neutral to test papers.

When colourless indigo-red is heated in vessels containing air, it

melts and turns yellow, but crystallises again on cooling; when more strongly heated, it melts, boils, and partly decomposes, without however giving off an acid or ammonia. Heated in free contact with the air, it smokes, burns with a bright smoky flame, and leaves a trace of difficultly combustible charcoal. It dissolves in fuming nitric acid and forms a beautiful purple-red solution, which becomes yellow from decomposition; the solution is then identical with that obtained by dissolving indigo-red in nitric acid. Colourless indigo-red is immediately turned red by dilute nitric acid.

Colourless indigo-red forms two compounds with sulphuric acid, one soluble, the other insoluble in water. In cold sulphuric acid, it dissolves very slowly and but partially, imparting to it a lemon-yellow colour; the undissolved portion is of a burnt yellow colour; the same compound is precipitated by water from the yellow sulphuric acid solution. Concentrated hydrochloric acid also forms a similar insoluble burnt yellow compound; of this only a trace dissolves in the acid, to which it imparts a yellow colour; it is not precipitated by water. — Colourless indigo-red does not dissolve in water or in aqueous solutions of the alkalis, not even when they are boiling and highly concentrated. — It dissolves very slightly in acetic acid, from which it is not precipitated by water; in alcohol and in ether it dissolves slowly, with brownish yellow colour.

### 3. Indigo-brown.

CHEVREUL. *Ann. Chim.* 66, 5; also *Schw.* 5, 291.

BERZELIUS. *Schröb.* 3, 685.

*Resinous Indigo-green.* Discovered by Chevreul, in indigo from Guatemala and Java; more completely investigated by Berzelius, who found it in all kinds of indigo.

*Preparation.* 1. Powdered indigo is repeatedly boiled with water, and the solution evaporated to a small bulk. The reddish syrup thus obtained, is extracted with alcohol of 36° B.; water is added to the red alcoholic solution; and the alcohol distilled off. The indigo-brown, which is combined with ammonia, and remains dissolved in the aqueous solution, is precipitated by exactly neutralising the ammonia with sulphuric acid; then washed on a filter with a little water, dissolved off with alcohol, and the solution evaporated. (Chevreul.) It retains some of the sulphuric acid by which it was precipitated, and also indigo-blue. (Berzelius.) — 2. Powdered commercial indigo is extracted with sulphuric, hydrochloric, or acetic acid, and afterwards with water, then gently heated with concentrated potash-ley, which causes it to swell up to a light black paste; and the dark brown alkaline solution is filtered off without washing, since the dilute liquid would take up indigo-blue. The alkaline solution is slightly acidulated with sulphuric acid, and filtered (the yellowish-brown filtrate neutralised with carbonate of lime and evaporated, yields a little more indigo-brown when treated with alcohol); the precipitate, which is bulky, half gelatinous, and almost black, owing to an admixture of indigo-blue, is washed out with water and dissolved in carbonate of ammonia; the solution is evaporated to dryness; and the residue is dissolved in water, and filtered from the undissolved

portion, which consists of blue indigo mixed with a little indigo-brown, without washing out, since the residue would then dissolve. The indigo-brown is precipitated from the filtrate by sulphuric acid; the precipitate while still moist is digested with carbonate of baryta and water, whereby an insoluble and a sparingly soluble compound of indigo-brown with baryta are formed; and the solution is filtered and evaporated. Indigo-brown is thus obtained in combination with a little baryta; it seems impossible to obtain it perfectly pure. (Berzelius.)

*Properties.* Indigo-brown (2) forms a brown, shining, transparent varnish, which is almost colourless and neutral to test papers; (1) has a green colour (arising, according to Berzelius, from an admixture of indigo-blue).

*Decompositions.* 1. Indigo-brown (2) yields by dry distillation, a black viscid oil, and colourless, highly ammoniacal water. — 2. Heated in contact with the air, it softens, swells up, and evolves fumes, smelling like burnt animal matter; then burns with flame, and leaves a residue of difficultly combustible charcoal containing carbonate of baryta. — 3. It dissolves in nitric acid with evolution of nitrous fumes, and forms a yellow turbid solution, from which water precipitates burnt-yellow flakes, which give a dark yellow solution with ammonia. The aqueous solution first deposits crystals of oxalic acid on evaporation, and when of the consistence of syrup, solidifies into a flaky crystalline mass, which tastes first acid and then bitter. When neutralised with potash, it yields crystals of nitre and of a burnt-yellow bitter substance, which is deliquescent, soluble in alcohol, and swells up when heated without exploding. — 4. Chlorine gas passed through a solution of indigo-brown, turns it to a paler colour, and then precipitates brownish yellow flakes of hydrochlorate of indigo-brown, but does not produce any further decomposition. (Berzelius.)

*Combinations.* Indigo-brown (1) is slightly soluble in water. — That prepared according to (2), combines very readily with *acids*, forming compounds which are slightly soluble in water. When an alkaline solution of indigo-brown is treated with an excess of acid, a compound of indigo-brown with the acid is precipitated, which is brown, very bulky, transparent only when viewed in thin layers, reddens litmus after it has been washed with water, and is very slightly soluble in water, to which it imparts a yellow colour. The precipitates produced by sulphuric acid and hydrochloric acid, colour boiling water yellow, and shrink up to a brittle mass, which may be pulverised in the solution. (Berzelius.) According to Chevreul, (1) dissolves in aqueous solutions of acids more readily than in water, and likewise in sulphuric acid, forming a green solution.

✱ Indigo-brown (2) unites readily with alkalis, and forms very dark-brown compounds, which are soluble in water, and do not show any alkaline reaction with reddened litmus paper. — When the solution of indigo-brown in carbonate of *ammonia* is evaporated, and the residue dried at 70°, it forms a black shining mass, which splits up into long needle-shaped fragments; has a slight and very unpleasant taste; evolves large quantities of ammonia when treated with potash, but no carbonic acid when treated with acids; it dissolves readily in water and somewhat less in alcohol. (Berzelius.) According to Chevreul, (1) dissolves in

ammonia, forming a red solution. When the solution of indigo-brown (2) in aqueous *potash* is exactly neutralised with acetic acid, the liquid evaporated to dryness, and the acetate of potash extracted by alcohol (which takes up a little indigo-brown), the compound of indigo-brown with potash remains behind. This compound dissolved in water and evaporated to dryness, forms a black shining mass, which splits up into needle-shaped fragments. — The *baryta*-compound is difficultly soluble in water. — The *lime*-compound is insoluble: hence lime-water precipitates indigo-brown from its ammoniacal or potash solution; and when hydrate of lime is boiled with a solution of indigo-brown in potash, it removes the former so completely, that a colourless ley remains behind. The solutions of (2) in alkalis or acetic acid form dark precipitates with acetate of lead, subacetate of lead and ferric sulphate; they are not precipitated by ferrocyanide of potassium and corrosive sublimate, nor, with the exception of the baryta compound, by infusion of galls. (Berzelius.)

Indigo-brown (2) treated with a little *acetic acid*, forms two compounds, the one soluble, the other insoluble in water. The first is obtained by acidulating with acetic acid a solution of indigo-brown in potash, so that it decidedly reddens litmus; the solution is then evaporated to dryness, and the acetate of potash extracted with alcohol. This compound reddens litmus, and dissolves very readily in water, from which it is not precipitated by boiling; it is slightly soluble in alcohol, but when boiled with the latter, becomes almost insoluble in water. The more acid compound is precipitated by strongly supersaturating the potash solution with acetic acid; when washed with water, a small portion is converted into the first compound; the wash-water continues to dissolve the precipitate, but becomes turbid when mixed with the first acid filtrate. (Berzelius.)

Indigo-brown (1) readily forms with alcohol, even when cold, a solution which appears green by reflected light, and red by transmitted light; it is not rendered turbid by water, but becomes green, and on the addition of a little ammonia, red. (Chevreul.)

The green thick oily substance extracted from fresh woad, by Chevreul (*Schw.* 5, 310), behaves in a similar manner; it diffuses an aromatic and empyreumatic odour when placed on glowing charcoal, and leaves a residue of tumefied charcoal. It is almost insoluble in water, is coloured red by alkalis, and becomes green again on the addition of an acid.

According to Hervy (*J. Pharm.* 26, 293), a substance similar to indigo-brown is obtained from *Polygonum tinctorium*. The fresh leaves are bruised and exhausted with cold water, and the reddish solution is filtered and evaporated to dryness. A yellow colouring matter is extracted by ether from the residue, the remainder of which is dissolved in alcohol of 40°, filtered, and evaporated to dryness. The product is rose coloured, and dissolves with green colour in dilute acids; in concentrated acids it turns green without dissolving. It dissolves in alkalis, with evolution of ammonia. It is soluble in water, from which it is precipitated green by concentrated acids; also in alcohol, but not in ether.

When an aqueous solution of indican, which has become brown by long boiling, is boiled with sulphuric acid or hydrochloric acid, dark brown flakes separate out, and may be washed on a filter with water. The precipitate boiled with alcohol, forms a brown solution which leaves on evaporation, a dark brown, shining, resinous residue of *Indikumin*. This substance melts in boiling water, is decomposed and



dissolved by boiling nitric acid, and dissolves with brown colour in ammonia; the ammoniacal solution forms brown precipitates with chloride of calcium and chloride of barium, and the alcoholic solution is completely precipitated by acetate of lead. The composition of indihumin corresponds most nearly to the formula  $C^{16}NH^6O^6$ . (Schunck, *N. Phil. Mag. J.* 10, 86.)

### Isatin.



LAURENT. *Compt. rend.* 12, 539; *J. pr. Chem.* 24, 2; *Pharm. Centr.* 1841, 601; *N. Ann. Chim. Phys.* 3, 371; *J. pr. Chem.* 25, 434; *Ann. Pharm.* 48, 262; *Pharm. Centr.* 1842, 246; *Rev. scient.* 10, 295, 300; 18, 458; *J. pr. Chem.* 35, 108.

ERDMANN. *J. pr. Chem.* 24, 11; *Pharm. Centr.* 1841, 707.

A. W. HOFMANN. *Ann. Pharm.* 53, 11.

Discovered simultaneously by Laurent and Erdmann, in 1841.

**Formation.** By the action of nitric acid or chromic acid upon indigo-blue (p. 42).

**Preparation.** 1 kilogr. of finely powdered good commercial indigo is stirred up in a large dish to a thin paste with water; it is then placed over a moderate fire, and commercial nitric acid is gradually added (which causes a violent effervescence, without evolution of nitrous acid), until the blue colour has disappeared, for which, from 600 to 700 grm. of nitric acid are necessary. The solution is boiled with several quarts of water, and filtered boiling as rapidly as possible; after 12 hours the isatin separates in reddish crystalline nodules. The mother-liquor is boiled with the undissolved residue and filtered, the operation being two or three times repeated: the last mother-liquor still yields isatin on evaporation. The crystals are moistened with water containing a little ammonia, in order to remove a resinous matter; they are then washed with cold water, and finally recrystallised several times from boiling alcohol (100 pts. of indigo yield 18 pts. of isatin). (Laurent.) — When an excess of nitric acid is employed, nitrosalicylic acid is formed. After each addition of nitric acid, it is necessary to wait until the effervescence is over. If no effervescence takes place, in consequence of the indigo being mixed with too much water, and if the boiling is continued, whilst more and more nitric acid is added, a violent reaction suddenly ensues when the solution has reached a certain concentration, the mass overflowing the vessel even when it is very capacious, and the residue contains generally nitrosalicylic acid. (Hofmann.) — 2. Indigo is heated with chromic acid, properly diluted, until the whole nearly boils, when it is filtered hot; isatin then crystallises out on cooling, and is purified by repeated recrystallisation from water and lastly from alcohol. If the chromic acid is so concentrated that it causes an evolution of carbonic acid, the solution deposits little or no isatin on cooling, but a small quantity on spontaneous evaporation or in vacuo; on evaporating the solution by heat, only sesquioxide of chromium and a brown powder separate. (Erdmann.) Laurent drops a dilute aqueous solution of chromic acid upon powdered indigo, and warms the mixture, the addi-

tion of chromic acid being discontinued as soon as the blue colour has disappeared, and the process continued as in (1). In order to purify crude isatin which still contains resin, Hofmann dissolves it in potash, and carefully adds hydrochloric acid to the solution, as long as it forms a black or brown precipitate; when a portion on filtering is of a pure yellow colour, and gives a deep red precipitate with hydrochloric acid, the whole solution is filtered off, decomposed with hydrochloric acid, and the precipitate washed with a little water.

*Properties.* Isatin crystallises in large transparent brownish red prisms, or in smaller yellowish red prisms, belonging to the right prismatic system; the crystals are very brilliant, especially when obtained from an alcoholic solution.  $\infty P. \infty \check{P} \infty. \check{P} \infty$ ; (Fig. 65) with predominating faces  $t; u' : u = 133^\circ 50' - 55'$ ;  $i : i' = 127^\circ 15' - 30'$ , G. Rose;  $\infty P. \infty \check{P} \infty. \bar{P} \infty$ ; (fig. 68) without  $p$  and  $i$ ;  $u' : u = 45^\circ 56'$ ;  $y : y = 126^\circ 44'$ . (Schabus.) Isatin is inodorous and has a bitter taste. (Schabus.) It melts when heated, and solidifies on cooling into a crystalline mass of needles; when heated above its melting point in contact with the air, the greater part volatilises without decomposition, in yellow and very irritating vapours.

					Erdmann.		Laurent.
16 C	.....	96	...	65.31	.....	65.61	.... 65.13
N	.....	14	...	9.52	.....	9.44	.... 9.50
5 H	.....	5	...	3.41	.....	3.43	.... 3.53
4 O	.....	32	...	21.76	.....	21.52	.... 21.84
<hr/>							
$C^{16}NH^5O^4$	.....	147	...	100.00	.....	100.00	.... 100.00

*Decompositions.* Isatin distilled in a retort, leaves a large residue of charcoal. (Erdmann, Laurent.) When thrown upon glowing charcoal, it diffuses the same odour as indigo. Heated in the air upon platinum foil, it burns with a brilliant flame, and leaves a fused residue of difficulty combustible charcoal. (Erdmann.) — 2. When isatin is suspended in hot water, and a current of chlorine passed through the solution, it is converted into chlorisatin; no bichlorisatin is formed, even if the solution is exposed to sunshine. (Erdmann.) Chlorine gas passed into a solution of isatin in potash-ley, produces a brown tarry liquid soluble in alcohol, but no bichlorisatin. (Hofmann.) — 3. Isatin shaken up with bromine-water, in sunshine, yields bromisatin; in contact with anhydrous bromine in sunshine, it forms bibromisatin. (Erdmann, Laurent, Hofmann.) — 4. Moderately warm nitric acid dissolves isatin without decomposition, but on boiling, a violent action takes place, attended with evolution of nitrous fumes, oxalic acid being formed together with a reddish brown resin, which contains  $NO^4$  and is soluble in ammonia; no picric acid is formed. (Laurent.) — 5. Isatin heated with fuming sulphuric acid, dissolves with brownish red colour; a strong effervescence then takes place, and on treating the solution with water and alcohol, a yellow substance is obtained, which has not been further investigated. (Laurent.) — 6. Isatin dissolves in cold potash without undergoing decomposition, and imparts to it a brownish red-colour; after a time, or immediately on boiling, the solution becomes yellow and is found to contain isatate of potash:  $C^{16}NH^5O^4 + 2HO = C^{16}NH^7O^6$  (Laurent, Erdmann). On pouring cold potash on crystals of isatin, they first turn dark red, and on warming the

whole, an orange-yellow solution of isatate of potash is formed; if this solution is concentrated by distillation, a reaction suddenly takes place, colourless drops of aniline passing over with the steam, while hydrogen is at the same time evolved:



(Hofmann.) — 7. *Ammonia* forms with solutions of isatin, various products of decomposition, which vary according to the concentration of the ammonia and the solvent of the isatin; mixtures of various compounds are always formed, all of which contain 1, 2, or 3 atoms of isatin, *plus* 1 or 2 atoms of ammonia, *minus* water. (Laurent.) Aniline behaves in the same way. (Engelhardt.) — Isatin with sulphurous acid in the presence of alkalis, forms salts of isatosulphurous acid. (Laurent.) Isatin dissolves in sulphite of ammonia with formation of *isatyde*. (Erdmann.) — 9. When a stream of *sulphuretted hydrogen* is passed through an alcoholic solution of isatin, *bisulphisatyde* ( $\text{C}^{32}\text{N}^2\text{H}^{12}\text{O}^4\text{S}^2$ ) is formed. (Erdmann, Laurent.)

*Combinations.* Isatin dissolves slightly in cold water, and more abundantly in boiling water. The solution is of a dark reddish-yellow colour.

It dissolves when gently warmed with nitric acid, and crystallises unchanged from the solution on cooling.

*Metallic Isatides.* — Isatin forms with the metals, compounds in which 1 At. hydrogen of 1 At. isatin, is replaced by a metal ( $\text{C}^{16}\text{NH}^4\text{MO}^4$ ). (Laurent.)

*Isatide of Ammonium* is formed by dissolving powdered isatin in ammonia, with which it forms a carmine-red solution. Acids precipitate isatin from this solution, and nitrate of silver forms a carmine-red precipitate. (Laurent.)

*Isatide of Potassium* is formed by dissolving isatin in cold potash. The solution is of a dark violet colour, which, when diluted with water and boiled, becomes pale yellow, and then contains isatate of potash.

Isatide of ammonium forms with salts of iron, cobalt and lead, precipitates which are mixtures of isatin with the oxides.

A boiling solution of isatin, to which a little ammonia is added, forms with protochloride of tin, a white precipitate, which becomes of a beautiful carmine-red on boiling. The filtrate is rose-coloured, but turns yellow in a few seconds; the precipitate on the filter is rose-coloured. (Laurent.)

*Isatide of Cuprammonium* forms a bright brown precipitate, which is obtained by mixing an ammoniacal solution of isatin with a solution of acetate of copper in ammonia. It contains 28.0 per cent. of copper, and is therefore  $\text{C}^{16}\text{N}^2\text{H}^6\text{Cu}^2\text{O}^4 = \text{C}^{16}\text{NH}^2(\text{NH}^4)\text{Cu}^2\text{O}^4$ ; or, according to Laurent,  $\text{C}^{16}\text{NH}^4(\text{NH}^2\text{Cu}^2)\text{O}^4$ , which would require 28.08 per cent. copper. It forms a precipitate with hydrochloric acid and bichloride of platinum. (Laurent.)

*Isatide of Silver.* 1. An alcoholic solution of isatin is mixed with an alcoholic solution of nitrate of silver, and an alcoholic solution of



potash is added, in such proportion, that an excess of isatin and nitrate of silver may remain in solution. The wine-red precipitate is filtered, washed and dried. — 2. Nitrate of silver is poured into a slightly ammoniacal alcoholic solution of isatin. (Laurent.)

				Laurent.	
				1.	2.
$C^{16}NH^8O^4$ .....	146	....	57.48		
Ag .....	108	....	42.52	42.5	42.2
<hr/>					
$C^{16}NH^8AgO^4$ .....	254	....	100.00		

*Isatide of Argentammonium.* When an ammoniacal alcoholic solution of isatin is poured into an alcoholic solution of nitrate of silver to which a large excess of ammonia has been added, a red crystalline precipitate is immediately formed, consisting of microscopic pearly flakes. (Laurent.)

				Laurent.
16 C .....	96	....	35.42	35.23
2 N .....	28	....	10.33	
7 H .....	7	....	2.58	2.66
Ag .....	108	....	39.85	39.75
4 O .....	32	....	11.82	
<hr/>				
$C^{16}NH^8(NH^4)AgO^4$ .....	271	....	100.00	

According to Laurent, the formula is  $C^{16}NH^8(NH^4Ag)O^4$ .

Isatin is readily soluble in *alcohol*, less so in *ether*. (Erdmann, Laurent.)

### Isatic Acid.



LAURENT. *Compt. rend.* 12, 539; *N. Ann. Chim. Phys.* 3, 376; *J. pr. Chem.* 25, 435; *Pharm. Centr.* 1841, 601; 1842, 247; *Ann. Pharm.* 48, 264.

ERDMANN. *J. pr. Chem.* 24, 13; *Ann. Pharm.* 48, 204; *Pharm. Centr.* 1841, 708.

Discovered simultaneously by Laurent and by Erdmann, in 1841.

*Formation* (p. 52).

*Preparation.* When isatate of lead is suspended in water and decomposed by sulphuretted hydrogen, the solution filtered from the sulphide of lead and evaporated in vacuo yields a white, flocculent, scarcely crystalline powder, perfectly soluble in water. The colourless solution when heated, immediately becomes brownish yellow and deposits crystals of isatin. (Erdmann.)

The formula of the *isatates* is  $C^{16}NH^8MO^6$ .

\* According to the system of classification adopted in this work, isatic acid should be placed among compounds derived from the primary nucleus  $C^{16}H^{10}$ .

A solution of isatate of ammonia, obtained by decomposing isatate of potash with sulphate of ammonia, yields isamate of ammonia on evaporation. (Laurent.)

*Isatate of Potash.* — When isatin is dissolved in a cold strong solution of potash, and the dark-red solution is diluted with water, boiled till it becomes pale yellow, and then evaporated, pale yellow crystals of the potash-salt are deposited. The solution of the salt in water or alcohol forms no precipitate on the addition of hydrochloric acid, but becomes red after a time, or immediately on boiling, and if left in a cool place, deposits crystals of isatin.

*Isatate of Baryta.* — 1. Chloride of barium is precipitated only by an extremely concentrated solution of isatate of potash. — 2. Isatin is boiled with baryta water, and the solution filtered; on evaporating the filtrate, small crystalline flakes are obtained, which are slightly soluble in water and almost insoluble in alcohol. (Laurent.) The white flakes precipitated by the potash-salt in a solution of chloride of barium, dissolve on heating the liquid, and the solution deposits short colourless prisms on cooling. (Erdmann.) The salt contains 53·24 per cent. baryta when dried at 150°, and corresponds to the formula  $C^{16}NH^6BaO^6$ . (Laurent.)

The aqueous solution of the potash-salt does not precipitate solutions of chloride of strontium, chloride of magnesium, chloride of calcium, alum, zinc-salts, protochloride of tin, chloride of cadmium, chloride of cobalt, chloride of nickel, or chloride of mercury; with uranic nitrate, it produces an orange-yellow precipitate which in a few minutes becomes scarlet. It precipitates sesquichloride of iron reddish brown, and acetate of lead in yellow flakes. (Laurent.) According to Erdmann, the lead precipitate is white, and incompletely soluble in boiling water. Isatate of potash forms with sulphate of copper, a green solution from which green flakes precipitate, but dissolve again on heating, or on the addition of more water. Heated with acetate of copper, it forms a yellowish green precipitate, which redissolves on cooling. Mercurous nitrate is precipitated yellow.

*Isatate of Silver* is precipitated on mixing an aqueous solution of the potash-salt with nitrate of silver, as a white or pale yellow substance, which dissolves in boiling water and becomes partially blackened. The solution, on cooling, deposits crystalline flakes and grains. When nitrate of silver is dropped into a lukewarm aqueous solution of isatate of potash, a portion is immediately precipitated, but the greater part crystallises on cooling in minute, shining, straw-coloured laminæ, united in tufts. (Erdmann.) When boiling solutions of isatate of potash and nitrate of silver are mixed together, beautiful yellow prisms of the silver salt crystallise out on cooling. (Laurent.)

	At 140°			Laurent.		Erdmann.	
16 C .....	96	...	35·29	.....	35·32	...	35·18
N.....	14	...	5·15				
6 H.....	6	...	2·21	.....	2·48	...	2·30
Ag .....	108	...	89·70	.....	38·40	...	37·50 to 41·05
6 O.....	48	...	17·65				
<hr/>							
$C^{16}NH^6AgO^6$ .....	272	...	100·00				

### Isatosulphurous Acid.



LAURENT. (1842.) *Compt. rend.* 14, 490; *J. pr. Chem.* 26, 123; *Rev. scient.* 9, 30; 10, 289; *J. pr. Chem.* 328, 336; *Pharm. Centr.* 1843, 257.

Isatosulphurous acid is not known in the free state, but only in its salts, the *isatosulphites* : for when these salts are treated with a stronger acid, the isatosulphurous acid is decomposed.

The formula of the isatosulphites is  $C^{16}NH^8MO^6, 2SO^2$ . — (For their formation see p. 53.)

*Isatosulphite of Ammonia.* — Powdered isatin is boiled with bisulphite of ammonia till the isatin is dissolved ; the solution is evaporated till it begins to crystallise; and the crystals are purified by recrystallisation. Small pale yellow rhombic tables. — The crystals do not lose weight at  $100^\circ$  or in vacuo. — Isatosulphite of ammonia is not decomposed by excess of ammonia. When acted upon by chlorine, it forms chlorisatin and bichlorisatin, and the filtered solution forms with chloride of barium a quantity of sulphate of baryta corresponding to 2.68 per cent. of sulphurous acid : the formula  $C^{16}NH^8(NH^4)O^6, 2SO^2$  requires 27.58 per cent. It is more slowly decomposed by hydrochloric acid than the potash-salt. It forms with nitrate of silver, a precipitate which is a mixture of isatin and sulphite of silver. — It dissolves slightly in cold water, but very easily in hot water.

*Isatosulphite of Potash.* — 1. An aqueous solution of isatate of potash is saturated with sulphurous acid, evaporated and allowed to cool ; and the mother-liquor from the first crystals is evaporated down and left to crystallise. — 2. Powdered isatin is boiled with an aqueous solution of bisulphite of potash until all the isatin is dissolved, and the solution is evaporated down and left to crystallise. The salt is more easily obtained pure by the first method. — It forms rather long, pale yellow, and very brilliant crystals. — Perhaps fig. 43;  $a : a' = 148^\circ 30'$ ;  $a : t = 106$ ;  $t$  is rectangular; according to Laurent, it belongs to a peculiar system. The crystals lose from 10.4 to 11.9 per cent. of water, or four atoms at  $100^\circ$  (calculated 11.2 per cent.); and at the temperature at which they soften and become yellowish red, from 14.4 to 15 per cent. of water (5 At.).

	I.	
KO .....	47.2	18.93
16 C.....	96	38.52
N .....	14	5.61
4 H .....	4	1.60
3 O .....	24	9.61
2 SO <sup>2</sup> .....	64	25.73
<hr/>		
$C^{16}NH^8KO^6, 2SO^2$ .....	249.2	100.00

	II.		Laurent.
KO .....	47.2	17.66	17.75
16 C .....	96	35.94	36.48
N .....	14	5.24	
6 H .....	6	2.24	1.99
5 O .....	40	14.97	
2 SO <sup>2</sup> .....	64	23.95	24.85
<hr/>			
C <sup>16</sup> NH <sup>6</sup> KO <sup>6</sup> ,2SO <sup>2</sup> .....	267.2	100.00	

According to Calculation ii, (Gerhardt, *Tr.* 3, 546,) isatin takes up the elements of two atoms of water in the formation of isatosulphurous acid; Laurent first assumed the formula C<sup>16</sup>NH<sup>6</sup>MO<sup>6</sup>,2SO<sup>2</sup>, for the dry salt, and afterwards (*Rev. scient.* 18, 458) C<sup>16</sup>NH<sup>4</sup>MO<sup>4</sup>SO<sup>2</sup> (Calculation i), and supposed that the salt which he analysed was not dried sufficiently.

	Crystallised.		Laurent.
C <sup>16</sup> NH <sup>6</sup> KO <sup>6</sup> .....	203.2	65.06	
2 SO <sup>2</sup> .....	64	20.53	21.56
5 HO .....	45	14.41	14.04
<hr/>			
C <sup>16</sup> NH <sup>6</sup> KO <sup>6</sup> ,2SO <sup>2</sup> + 5HO ....	312.2	100.00	15.0

When the crystallised salt is heated, it first becomes orange-yellow, then yellowish red, gives off water and softens. On further heating, it swells up, blackens, and yields a thick red substance, which solidifies on cooling without becoming crystalline.—When boiled with iodine, it forms isatin and sulphuric acid.—With chlorine, it forms sulphuric acid and chlorisatin,—also bichlorisatin, if the action of the chlorine be continued long enough.—Cold hydrochloric acid acts slowly upon it; the solution, however, becomes orange-yellow and smells of sulphurous acid, and if sufficiently concentrated, deposits in a few minutes crystals of isatin. If hydrochloric acid is added to the boiling solution of the salt, sulphurous acid is immediately evolved with effervescence, and isatin is precipitated. The hot solution of the salt becomes darker coloured on the addition of sulphide of ammonium, and deposits, on cooling, a yellowish powder, consisting of microscopic needles which react like isatyde. They are insoluble in water and in alcohol, and when thrown upon glowing charcoal, smell like indigo and not at all sulphurous. When heated upon platinum foil, they become violet-red, probably owing to the formation of indin, since they then form with concentrated alcoholic potash, a solution yielding a black salt which is decolorised by a gentle heat. The needles dissolve in potash, forming a wine-red solution which loses its colour when boiled, and becomes yellow on boiling with hydrochloric acid, while isatin is produced, together with a soft substance which forms a film upon the solution.—Isatosulphite of potash dissolves pretty readily in water, to which it imparts a yellow colour; the solution becomes brownish-red on the addition of ammonia, but regains its yellow colour when boiled, and then contains sulphite of potash, sulphite of ammonia and isatin dissolved in ammonia.—It does not precipitate the chlorides of barium, strontium and calcium, or acetate of copper.—With acetate of lead, it forms a yellow precipitate of isatin and sulphite of lead; with an aqueous solution of nitrate of silver, it forms a precipitate of isatin and sulphite of silver, whilst the solution contains nitrate of potash and free nitric acid:



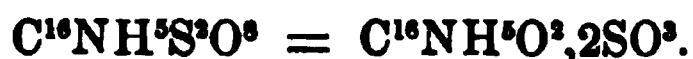
Can free nitric acid and sulphite of silver exist together? Gm.

A carmine-red precipitate is formed by mixing an aqueous solution of the potash-salt with ammoniacal nitrate of silver, or by gently heating nitrate of silver with ammonia and isatin.

The potash-salt is very slightly soluble in cold alcohol, but moderately soluble in boiling alcohol, to which it imparts a yellow colour.

*Conjugated Compounds of the nucleus  $C^{16}NH^5O^3$ .*

**Sulphindigotic Acid.**



BERGMANN. *Opusc.* 5, 7, 1788.

HAUSMANN. *J. Phys.* 1788, March.

BUCHOLZ. *A. Gehlem.* 3, 3.

W. CRUM. *Ann. Phil.* 1823, Febr.; *Schw.* 38, 35.

BERZELIUS. *Schr.* 4th ed. 3, 706; *Pogg.* 10, 105; *Jahresber.* 7, 256.

JOSS. *Schw.* 69, 285; *Pharm. Centr.* 1834, 167.

DUMAS. *N. Ann. Chim. Phys.* 2, 204; *J. pr. Chem.* 24, 200; *Pharm. Centr.* 1841, 597.

*Sulphate of indigo, Soluble blue indigo, Sulphindylie acid, Indigblauschwefelsäure, Cærulinschwefelsäure.*

*Formation.* — (p. 43.)

*Preparation.* To a solution of indigo-blue in excess of hot sulphuric acid 50 parts of water are added, and the liquid is filtered from the precipitated sulphophœnicic acid; the filtrate is digested at a gentle heat with wool or woollen stuff (previously prepared by washing, first with soap and then with water containing 1 per cent. carbonate of soda, and finally with pure water), until no more colouring matter is taken up (the excess of sulphuric acid remaining in solution); the wool, dyed blue by sulphindigotic and hyposulphindigotic acids, is washed with water till the latter no longer becomes acid, and is then digested with water containing a little carbonate of ammonia; the blue solution is poured off from the decolorised wool and evaporated to dryness at  $50^\circ$ ; and the residue is exhausted with alcohol of 0.833 per cent., which dissolves the hyposulphindigotate of ammonia, and leaves behind the sulphindigotate of ammonia. The latter is dissolved in water and precipitated by acetate of lead; the dark blue precipitate is washed with water, then suspended in water, and decomposed by sulphuretted hydrogen; and the yellow or colourless solution, which turns blue on exposure to the air, is evaporated to dryness at  $50^\circ$ . (Berzelius.) According to Joss, sulphindigotate of ammonia is not effectually separated from hyposulphindigotate of ammonia by alcohol; it is better, therefore, to digest the indigo solution with wool only so long as it forms a precipitate with acetate of baryta, by which hyposulphindigotic acid is not precipitated.

*Properties.* Sulphindigotic acid forms a solid mass having a peculiar agreeable odour and an acid taste; it has a weak but decided acid reaction. (Joss.)

*Decompositions.* — 1. Sulphindigotic acid yields by dry distillation, sulphurous acid, sulphite of ammonia, much water, and a little empyreumatic oil. No vapours of indigo-blue are evolved, but the sublimed sulphite of ammonia dissolves in water with a blue colour, having carried over a little of the undecomposed acid. The carbonaceous residue burns with difficulty, but completely. The sulphindigotates also do not yield any sublimate of indigo by dry distillation. (Berzelius.) — 2. Sulphindigotic acid is decomposed by exposure to sunlight. — 3. Chlorine produces a quantity of brown resin in the solution of the acid, and only a little chlorisatin and bichlorisatin. (Erdmann, *J. pr. Chem.* 19, 355.) — The blue colour of the acid is changed to green by *chloride of lime* (Schlumberger), and to reddish brown by *chlorate of potash* and *hydrochloric acid*. (Bolley.) — 4. Sulphindigotic acid is decomposed by nitric acid. When the baryta-salt is decomposed by boiling with concentrated nitric acid and the solution diluted and filtered, it is not precipitated by chloride of barium. (Berzelius.) — 5. The solution of sulphindigotic acid, heated with *chromate of potash*, becomes ochre-yellow (Penny); mixed with permanganate of potash, it becomes first green and then brownish yellow (Elbers, Mohr); when heated with ferric salts it is decolorised as by nitric acid. (Wöhler, *Ann. Pharm.* 34, 235.)

The decolorising of the solution of sulphindigotic acid by oxidising agents is used to determine the amount of indigo-blue in commercial indigo. A weighed quantity of indigo is dissolved completely in fuming sulphuric acid, and the solution is diluted with water to a certain volume. A graduated solution of a substance capable of yielding oxygen or chlorine is then gradually added till the blue colour of the solution has disappeared, and the amount of the graduated solution employed is compared with the quantity of the same solution required to decolorise a solution containing a quantity of pure indigo-blue, or of a determined kind of commercial indigo, equal in weight to the indigo to be tested. According to Mohr, a graduated solution of permanganate of potash is the most suitable for this purpose. Bolley adds hydrochloric acid to the boiling solution of the acid, and then a graduated solution of chlorate of potash. — Penny adds hydrochloric acid to the gently warmed indigo solution, and then a solution of chromate of potash. — Lindenlaub adds sulphite of soda to the solution, and then adds chlorate of potash drop by drop; Schlumberger decomposes it by chloride of lime. (Compare Mohr, *Lehrb. der Titrimethoden*, p. 189.)

6. Sulphindigotic acid mixed with excess of caustic alkali, becomes first green and then yellow, even when access of air is prevented, being converted first into indigo-green and then into indigo-yellow: ammonia acts more slowly than potash or soda; the alkaline carbonates do not cause decomposition. (Berzelius.) — Sulphindigotic acid is first coloured green by the addition of ammonia, and after the lapse of a few hours becomes completely decolorised; carbonate of ammonia and caustic potash exert the same action. An aqueous solution of sulphindigotate of potash forms, with ammonia and carbonate of ammonia, a green solution which becomes colourless in closed vessels, but when exposed to the air recovers its green colour for a short time, and then again becomes colourless. With caustic potash and soda, it forms a blue solution which gradually becomes green and then colourless; with lime-water, it forms a green solution which becomes yellowish in closed vessels, and when exposed to the air turns green again for a short time. (Bergmann.) The salts of sulphindigotic acid are converted by the slow action of alkalis into salts



of sulphoviridic, sulphopurpuric, sulphoflavic, sulphofulvic, and sulphorufic acids. (Berzelius.) — 7. Substances which readily take up oxygen, reduce sulphindigotic acid to a compound derivable from white indigo, and change the colour of the solution to yellow. Hydrogen passed through sulphindigotic acid produces scarcely any perceptible change of colour; if, however, zinc or iron is dissolved in the acid, the solution becomes colourless in 24 hours with zinc, and pale blue with iron. Exposure to the air restores the blue colour, according to Holt; according to Pleischl (who must have continued the action for a longer time), it does not. (*Schw.* 25, 363.) — Protochloride of tin also reduces sulphindigotic acid with the aid of heat. — Sulphuretted hydrogen passed through the aqueous solution for several hours does not decolorise it; if, however, the solution be then heated to  $50^{\circ}$ , sulphur is precipitated and the blue colour disappears, provided sulphuric acid is not present in excess. If the decolorised solution containing an excess of sulphuretted hydrogen, is placed over slightly moistened potash in vacuo, a viscid dark yellow mass is obtained, which becomes moist on exposure to the air, and then rapidly assumes a dirty green, and finally a blue colour. (Berzelius.) Sulphindigotic acid is turned green, and afterwards yellow or colourless, by the following substances: — Sulphuretted hydrogen, pentasulphide of potassium, protochloride of iron, protosulphate of iron, tartaric acid, acetic acid, formic acid, tartrate of potash, sugar, madder, woad, &c.; at first the blue colour may be restored by air or by chlorine-water, but this can no longer be effected when the action of the deoxidising substances has been too long continued. — Sulphurous acid gradually turns sulphindigotic acid green, then yellow, and then almost colourless, but the blue colour cannot be restored by air or by alkalis. (Bergmann.) — Sulphindigotic acid becomes decolorised when exposed in sunlight to the joint action of sulphurous acid and atmospheric air; in the dark, the change takes place more slowly. Sulphurous acid alone does not so readily decolorise the acid. If a few drops of sulphindigotic acid are poured into a concentrated aqueous solution of sulphurous acid, the blue colour soon disappears and the mixture becomes brownish yellow; the blue colour is restored by heating, by oxidising substances, by sulphuretted hydrogen, or by sulphuric acid. Sulphites have a stronger decolorising action than the free acid; the colour is restored by the same reagents, with the exception of sulphuretted hydrogen, and especially by heat, but disappears again, as the solution cools. — An aqueous solution of sulphurous acid, which has been turned brownish yellow by the passage of an electric current, decolorises sulphindigotic acid more energetically than pure sulphurous acid or its salts; the above-mentioned brown solution when saturated with a base, has the same action as the solution itself. — The decolorising property is destroyed by oxidation in the air, by sulphuretted hydrogen, or by oxidising agents. — When zinc filings (or iron filings) are allowed to digest with an aqueous solution of sulphurous acid out of contact with the air, till the solution has become brownish yellow (or again colourless by the prolonged action of the zinc), it possesses in the highest degree the property of decolorising sulphindigotic acid. This property is not destroyed by heat, but readily by oxygen (which liberates sulphurous acid from the solution, even when it is saturated with oxide of zinc); also by easily reducible oxides, and by iodine, bromine, chlorine, ozone, sulphuretted hydrogen, arsenious acid, tartar emetic, hydrochloric acid, sulphuric acid, and phosphoric acid. If the zinc be precipitated by carbonate of ammonia

from the decolorising solution of the zinc-salt, salts are obtained which decolorise sulphindigotic acid with extraordinary energy. The hyposulphites which are obtained by the process described in Vol. II. p. 160, 2 and 3, do not decolorise sulphindigotic acid. The blue colour is restored to the decolorised solution of sulphindigotic acid : *a.* By heat, sulphur being then precipitated. If the solution was saturated with oxide of zinc, and the sulphindigotic acid also neutralised by an alkali, it does not recover its blue colour either by warming or by exposure to the air. — *b.* By the oxygen of the air, or by oxidising agents. — *c.* By sulphuretted hydrogen. — Penta-sulphide of hydrogen,  $\text{HS}^5$ , decolorises sulphindigotic acid ; if the air be excluded the solution becomes blue again after a time. Caustic alkalis, or their carbonates produce the same reaction. (Schönbein, *J. pr. Chem.* 61, 203, 240.) — 8. When a solution of 1 part of indigo in 4 parts of sulphuric acid is diluted with 20 parts of water, filtered, and the liquid mixed with an equal volume of ether and heated to its boiling point for several hours in a sealed glass tube, it is gradually decolorised : the same action takes place when less ether is added to a more dilute solution of indigo. The blue colour is not restored, either by oxygen, or by oxide of copper, or by the oxides of the noble metals. The liquid has an ethereal odour, and yields by distillation a colourless liquid which reddens litmus, does not precipitate baryta-salts, and forms with nitrate of silver a precipitate soluble in ammonia. (Cassola, *Kastn. Arch.* 16, 126.) — Ether vapour passed into sulphindigotic acid sometimes decolorises it, but with difficulty and not always ; perhaps the action is due to the presence of aldehyde. (A. Vogel.) — 9. Sulphindigotic acid shaken up with aldehyde, becomes emerald-green, then pale green, and, in a few minutes, yellow. The blue colour is not restored, either by exposure to the air, or by simple boiling, or by oxide of mercury. (A. Vogel, *J. pr Chem.* 16, 315.)

*Combinations. With Water.* Sulphindigotic acid becomes rapidly moist on exposure to the air, and dissolves very readily in water, forming a dark blue liquid. (Berzelius, Joss.)

The *Sulphindigotates* ( $\text{C}^{16}\text{NH}^4\text{MO}^3, 2\text{SO}^3$ ) are formed by direct combination or by double decomposition. They cannot be obtained crystallised ; they are dark-blue, with a peculiar coppery lustre, and taste feebly saline and decidedly of indigo. The alkaline sulphindigotates are slightly soluble in cold water, and more readily in hot water ; the solution is blue by reflected, and red by transmitted light. — The sulphindigotates are more readily decolorised than the free acid, by all substances which reduce blue indigo, especially in the presence of free alkalis. Protosulphate of iron does not reduce a neutral sulphindigotate, even on warming ; not even when as much alkali is added as is necessary to precipitate the protoxide of iron ; but the slightest excess of alkali produces immediate decoloration, and on the addition of enough acid to neutralise the alkali, the blue colour is restored. Sulphide of potassium or calcium decolorises the solutions of the sulphindigotates, part of the sulphide being converted into sulphate. The reduced solution appears yellow when neutral, and burnt-yellow when alkaline. The neutral solution leaves, when evaporated in vacuo, a dark dry residue which appears dark yellow when pulverised, and becomes blue on exposure to the air for several days. The solution becomes rapidly blue on exposure to the air, the change being slow only when unchanged reduced matter is present. In this case the coloration is at first only superficial, and proceeds downwards as the



reducing substance becomes oxidised. Ferric and cupric salts turn the solution blue instantly, and are converted into salts of the lower oxides. The solution reduced by protochloride of tin deposits, on exposure to the air, a white powder which is a mixture of binoxide of tin and a product of decomposition which becomes green on exposure to the air.

Sulphindigotates when heated, give off water without melting. When strongly heated, they decompose, evolving free ammonia, carbonate of ammonia, cyanide of ammonium, a trace of volatile oil, and afterwards of carbonic acid, whilst a residue of metallic sulphide is left.

*Sulphindigotate of Ammonia* is prepared by the process described at page 58 (Berzelius); or by precipitating sulphindigotic acid, which should not be too dilute, with ammonia or a salt of ammonia. (Crum.) It reacts similarly to the potash-salt. It melts when heated and swells up, but is not decomposed, even by a pretty strong heat, and although it assumes a charred appearance, still dissolves completely in water forming a blue solution. When more strongly heated, it yields a sublimate of sulphite of ammonia. (Berzelius.) It dissolves in from 40 to 50 parts of cold water, and in a much smaller quantity of hot water (Crum), and is precipitated from the solution by the alkaline sulphates and some other salts, but much less completely than the potash-salt. It is not soluble in alcohol. (Crum, Berzelius.)

*Sulphindigotate of Potash. — Precipitated Indigo, Indigo-carmine, Blue-carmine, Soluble Indigo.* — When an aqueous solution of sulphindigotic acid is saturated with excess of carbonate of potash, the whole becomes gelatinous. — 1. The blue wool obtained as described at page 58, is exhausted with carbonate of potash instead of carbonate of ammonia; the solution evaporated to dryness; the hyposulphindigotate of potash extracted with alcohol; the residue dissolved in water; the excess of carbonate of potash neutralised with acetic acid; the solution evaporated to dryness; and the acetate of potash extracted by alcohol: the sulphindigotate of potash then remains behind. (Berzelius.) — 2. One part of indigo is dissolved in 10 pts. of common sulphuric acid; the solution after standing for 24 hours is diluted with 10 times its volume of water, and about a quarter neutralised with carbonate of potash, or mixed with any other potash salt, except the nitrate; and the precipitate of sulphindigotate of potash is collected on a filter, washed with water containing 1 per cent. of acetate of potash, and then with alcohol, which however does not completely remove the acetate of potash. It is finally dried and then shrinks together considerably. (Crum, Berzelius.)

3. One part of blue indigo obtained from the vat and purified in the manner described at page 38, is allowed to stand in a closed flask with 15 parts of sulphuric acid for three days at a temperature between  $50^{\circ}$  and  $60^{\circ}$ . The solution is then diluted with water and filtered, which removes every trace of sulphophœnicic acid; the filtrate is mixed with acetate of potash, separated from the precipitate thus formed and left to drain, again stirred up with acetate of potash and filtered; and this treatment is repeated once or twice more, till all the sulphate of potash is washed out. Finally the acetate of potash is removed by repeatedly washing the precipitate with alcohol, and the residue is then dried. The product is very small. (Dumas.)

Copper-coloured mass yielding a blue powder; blue by transmitted light. It rapidly absorbs moisture from the air (10 per cent. in 2 hours).

				Dumas.
16 C .....	96	....	38.53	..... 38.37
N .....	14	....	5.62	..... 5.60
4 H .....	4	....	1.60	..... 2.07
KO, SO <sup>3</sup> .....	87.2	....	34.99	..... 34.32
SO <sup>3</sup> .....	40	....	16.05	..... 16.10
O .....	8	....	3.21	..... 3.54
<hr/>				
C <sup>16</sup> NH <sup>4</sup> KO <sup>3</sup> , 2SO <sup>3</sup> .....	249.2	....	100.00	..... 100.00

Sulphindigotate of potash does not melt when heated or evolve any purple vapours : it is difficult to incinerate. According to Berzelius, it forms sulphopurpurate of potash when heated with lime-water out of contact with the air; in presence of air, it forms salts of sulphoflavic, sulphofulvic and sulphorufic acids.

Sulphindigotate of potash dissolves in 140 parts of cold water, and in a much smaller quantity of boiling water, a portion separating out on cooling. The solution is of a dark blue colour, transparent only when viewed in thin layers; when held up before the light of the sun or of a candle, it appears scarlet. 1 part of the salt imparts a blue colour to 500,000 parts of water. Water containing 1 per cent. of acetate of potash does not dissolve the salt in the cold; on heating, a portion dissolves and separates out in blackish flakes on cooling. It is readily dissolved by sulphuric acid, but is not soluble in concentrated hydrochloric acid (Crum); or in alcohol of sp. gr. 0.84. (Berzelius.)

If an aqueous solution of sulphindigotate of potash is mixed with a baryta or lime-salt and carbonate or phosphate of soda added, carbonate and phosphate of baryta and carbonate of lime are precipitated of a light blue colour, and phosphate of lime of a beautiful blue colour. When the solution of sulphindigotate of potash is mixed with acetate of lead and a solution of tannic acid, the precipitate of tannate of lead carries down all the colouring matter with it.

*Sulphindigotate of Soda* is prepared by precipitating sulphindigotic acid with pure carbonate, sulphate or acetate of soda or with chloride of sodium. The precipitate is washed with water containing 2 per cent. of acetate of soda. Sulphindigotate of soda reacts similarly to the potash-salt, but is less completely precipitated from its aqueous solution by other salts. When it is dissolved in hot water containing a soda salt, the greater part separates out in blackish grains on cooling. (Crum.)

*Sulphindigotate of Baryta* is precipitated in dark blue flakes, on mixing the potash-salt with chloride of barium. (Crum, Berzelius.) It dissolves slightly in cold water with a bluish colour; more abundantly in hot water, imparting to it a dark colour. Owing to the extraordinary affinity of baryta for sulphindigotic acid, this salt is formed when hyposulphindigotate of potash is mixed, first with sulphuric acid and then with chloride of barium; an excess of sulphate of baryta is, however, necessary to the reaction, and hence the precipitate has a paler colour. Sulphate of baryta already precipitated likewise forms with hyposulphindigotate of potash, a small quantity of sulphindigotate, and becomes

pale blue. (Berzelius.) — Dumas mixes a boiling aqueous solution of the potash-salt with excess of chloride of barium, filters while hot and washes the precipitate with boiling water; the salt crystallises on cooling. — It crystallises from an aqueous solution in large dark blue scales.

				Dumas.
16 C.....	96	....	34.46	..... 35.7
N.....	14	....	5.03	
4 H.....	4	....	1.43	..... 1.9
BaO, SO <sup>3</sup> .....	116.6	....	41.86	..... 41.4
SO <sup>3</sup> .....	40	....	14.35	
O.....	8	....	2.87	
<hr/>				
$C^{16}NH^4BaO^2, 2SO^3$ .....	278.6	....	100.00	

On heating sulphindigotate of baryta with lime-water, a salt of sulphoviridic acid is formed. (Berzelius.)

*Sulphindigotate of Lime.* — The solution of indigo in sulphuric acid is diluted with 50 times its volume of water, and neutralised by agitating with powdered marble. It is then filtered, and the precipitate, which is at first bright blue, is washed on the filter till it becomes red. After having been sufficiently evaporated, the solution is mixed with alcohol, when the salt precipitates in blue flakes which appear red by transmitted light. The precipitate is washed on a filter with alcohol. — After drying it has a purple colour. It dissolves more readily in water than gypsum, and separates from the solution, on evaporation, in blue flakes which dry up to a dark blue film inclining to purple. (Berzelius.)

*Sulphindigotate of Magnesia.* — This salt does not attract moisture from the air. It is readily soluble in water, and is not precipitated from its solution by an excess of a magnesia-salt: it is insoluble in alcohol. (Berzelius.)

*Sulphindigotate of Alumina.* — *a. Neutral.* — Readily soluble in water; dries up like the other sulphindigotates on the evaporation of the solution. — *b. Basic.* — Sulphindigotate of potash mixed with a salt of alumina and a little ammonia, forms a dark blue pulverulent precipitate which is blackish blue after it has been dried. The salt gives up all its acid to an excess of alkali. (Berzelius.)

*Sulphindigotate of Lead.* — *a. Neutral.* — The potash-salt forms with acetate of lead a precipitate of dark-blue flakes which are blackish blue after being dried. It is slightly soluble in water. — *b. Basic.* — The potash-salt forms with subacetate of lead, bright-blue flakes which become dark-blue on drying. (Berzelius.)

Sulphindigotic acid dissolves in *alcohol*.

Wool is dyed by aqueous sulphindigotic acid, but not by the salts of this acid, unless an acid, even a weak one like acetic acid, is added. Boiling water and alcohol deprive the wool of only a small portion of its colour, but alkalis remove it entirely. (Berzelius.) Sulphindigotic acid is completely decolorised by woollen stuffs; silk fabrics do not deprive it of all its colour, and linen and cotton take up very little. Silk

dyed with it is deprived of its colour by soap, but not by water. (Bergmann.)

Wood-charcoal, and more particularly blood-charcoal, takes up sulphindigotic acid from its aqueous solution, and yields it up again to alkaline carbonates. (Berzelius.)

### *Appendix to Sulphindigotic Acid.*

## 1. Hyposulphindigotic Acid.

BERZELIUS. *Lehrb.* 3, 711.

*Hyposulphocæruleic acid, Cærulinschwefelsäure.*

*Preparation.* The alcoholic solution of hyposulphocæruleate of ammonia obtained in the manner described at page 58, is mixed with an alcoholic solution of acetate of lead; the whole completely precipitated by a little ammonia, which also precipitates a basic salt; and the precipitated hyposulphindigotate of lead is treated like the sulphindigotate of lead (p. 58).

*Properties.* The acid, after being evaporated, appears completely dry at the edges, but soft in the middle. According to Berzelius, it has an acid taste; according to Joss, a cool, saline and not acid taste.

It exhibits the same decompositions as sulphindigotic acid.

*Combinations.* — *a.* It becomes slightly moist in contact with the air and dissolves readily in water.

*b.* The *hyposulphindigotates* exhibit the same characteristics as the sulphindigotates, with this exception, that they evolve sulphurous acid gas even at a gentle heat, the indigo-blue still remaining undecomposed. At a stronger heat, sulphite of ammonia sublimes, leaving a residue of a sulphide of the metal.

*Hyposulphindigotates of the Alkalis.* — Blue wool is extracted with a quantity of aqueous alkaline carbonate just sufficient for the purpose; the solution is evaporated to dryness; the residue extracted by alcohol; and the alcoholic solution evaporated. — The residue resembles the corresponding salt of sulphindigotic acid. It is readily soluble in water, from which it is precipitated in very small quantity by sulphuric acid and by other salts; it is also soluble in alcohol of sp. gr. 0.84. These salts are obtained less pure by mixing the solution of indigo in fuming sulphuric acid, after it has been diluted with water, with carbonates of the alkalis, the salt of sulphindigotic acid being then precipitated.

*Hyposulphindigotate of Baryta.* — A saturated solution of the potash-salt is precipitated by an excess of chloride of barium. — Dark blue flakes readily soluble in water; the solution when evaporated deposits a film having a coppery lustre.

*Hyposulphindigotate of Lime.* — *a. Neutral.* — The blue solution obtained by precipitating sulphindigotate of lime with alcohol is evaporated to dryness. The residue has a particularly beautiful coppery lustre, and dissolves readily in alcohol and in water. — *b. Acid.* — Hyposulphindigotate of calcium and lead, obtained by precipitating the alcoholic solution of the lime-salt with alcoholic acetate of lead, is suspended in water and decomposed by sulphuretted hydrogen. The filtrate reddens litmus feebly and does not taste acid.

*Hyposulphindigotate of Magnesia* does not attract moisture from the air; it is readily soluble in water and in alcohol, and is not precipitated from its aqueous solution by magnesia-salts.

*Hyposulphindigotate of Alumina* behaves like the sulphindigotate.

*Hyposulphindigotate of Lead.* — *a. Neutral.* — The alcoholic solution of the ammonia-salt is precipitated by an alcoholic solution of acetate of lead. Or a solution of indigo in sulphuric acid is saturated with carbonate of lead, filtered, and the precipitate washed with water as long as the filtrate is coloured blue. The solution is then evaporated; but the salt thus obtained contains a little sulphindigotate of lead. It forms a blue powder possessing an astringent, but not sweet taste. It dissolves slowly, but completely, in water. — *b. Basic.* — Prepared by precipitating the ammonia-salt with subacetate of lead.

*c.* Hyposulphindigotic acid behaves with wool, alcohol and charcoal in the same way as sulphindigotic acid. (Berzelius.) — Wool takes up a much smaller quantity of hyposulphindigotic than of sulphindigotic acid, and exhibits a less deep, but more fiery dye. (Jess.)

## 2. Sulphoviridic Acid.

BERZELIUS. *Lehrb.* 4th Ed. 7, 226.

Sulphoviridic acid is the first product of decomposition in the action of alkalis upon sulphindigotic acid.

1. To an alcoholic solution of an alkaline hyposulphindigotate, hydrate of potash is added in small portions until it becomes green, and the green precipitate is washed on a filter with a little alcohol. The precipitate is decomposed by an aqueous solution of oxalic acid, filtered, and the filtrate freed from excess of oxalic acid by triturating it with a little carbonate of lime: it is then filtered and evaporated to dryness.

2. When a solution of hyposulphindigotate of baryta is evaporated to dryness on a water-bath, it becomes green and yields a precipitate with subacetate of lead, but not with the neutral acetate; and if the greyish green precipitate is decomposed by sulphuretted hydrogen and the green filtrate evaporated to dryness, sulphoviridic acid is obtained as a dry, hard, gummy mass, having a strong acid reaction.

Its solution mixed with lime-water becomes yellow in contact with the air.

It dissolves very readily in water, and slowly, but completely, in strong alcohol; its solutions appear dark green by reflected light, and dark red by transmitted light. The lead-salt is somewhat soluble in water, imparting to it a greenish colour.

### 3. Indigo-green.

BERZELIUS. *LeArb.* 1828; 3, 728.

To an alcoholic solution of an alkaline hyposulphindigotate, hydrate of potash is added in small portions, until it becomes green, and the green precipitate is washed on a filter with a little alcohol. The precipitate is decomposed by an aqueous solution of oxalic acid, the liquid filtered, and the filtrate freed from an excess of oxalic acid by triturating it with a little carbonate of lime; it is then filtered and evaporated to dryness.

Indigo-green forms a green, solid residue.

It dissolves readily in water, forming a green solution, which when mixed with lime-water, becomes yellow on exposure to the air. It forms a green precipitate with acetate of lead, and does not precipitate corrosive sublimate or infusion of galls. (Berzelius.)

### 4. Sulphopurpuric Acid.

BERZELIUS. *Lehrb.* 4th Ed. 7, 227.

Formed by the action of alkalis upon sulphoviridic acid.

1 part of sulphindigotate of potash is dissolved in 50 parts of lime-water and heated in a covered vessel, till the solution, which has gradually turned purple-red, does not become green again on cooling. After the whole has been allowed to cool in the covered vessel, the excess of lime is precipitated by carbonic acid; the filtrate is evaporated to dryness; and the residue treated with alcohol, which extracts a little sulphoflavio acid. The residue is dissolved in water, the purple-red solution precipitated with acetate of lead, and the precipitate suspended in water and decomposed by sulphuretted hydrogen; the filtered solution is then evaporated to dryness.

Hard, brown, uncrystallised mass, dissolving in water with dark purple-red colour. The potash-salt dissolves in water and imparts to it a dark purple-red colour, like that of permanganate of potash. The precipitate produced by mixing the aqueous solution of the acid with acetate of lead, is slightly soluble in water, with a reddish colour; insoluble in alcohol. With excess of oxide of lead, a pale red salt is formed, which is insoluble in water.

## 5. Sulphoflavic Acid.

BERZELIUS. *Lehrb.* 4th Ed. 7, 228.

Formed by heating sulphoviridate of potash with lime-water in contact with the air.

Sulphindigotate of potash is heated with lime-water in an open vessel until the solution acquires a pure red colour (if the action is too prolonged it becomes yellow; if the access of air is kept under control, it is easier to hit the right moment). Carbonic acid is then passed through the liquid; the filtrate evaporated to dryness, and the green brownish yellow residue extracted with alcohol. The yellow solution is precipitated with acetate of lead; the lemon-yellow precipitate suspended in water and decomposed by sulphuretted hydrogen; and the solution filtered from the sulphide of lead, is then left to evaporate. It forms yellow arborescent masses, having a strong acid taste and reaction.

It is soluble in water and in alcohol: the solution forms with acetate of lead a lemon-yellow precipitate, insoluble in water.

## 6 and 7. Sulphofulvic and Sulphorufic Acids.

BERZELIUS. *Lehrb.* 4th Ed. 7, 229.

These acids are formed simultaneously with sulphoflavic acid.

The residue from which the sulphoflavic acid has been extracted by alcohol, is dissolved in water, and the beautiful red solution is precipitated with subacetate of lead. The pale-red precipitate is suspended in water and decomposed with sulphuretted hydrogen, and the filtrate is evaporated to dryness. Absolute alcohol extracts from the residue, *sulphofulvic acid*, which, on evaporation, is deposited as a dark yellow, transparent mass, having the consistence of an extract: it forms a lead-salt which is readily soluble in water and in alcohol. The portion insoluble in alcohol is *sulphorufic acid*. This latter dissolves in water with a fine red colour, and, on evaporating the water, forms a dark red, opaque, amorphous mass, which tastes acid and strongly reddens litmus. The lead-salt is readily soluble in water and in alcohol.

## 8. Indigo-yellow.

BERZELIUS. *Lehrb.* 1828; 3, 724.

Formed by heating hyposulphindigotate of lime with lime-water in contact with the air.

Hyposulphindigotate of lime is dissolved in lime-water, evaporated down till the solution has become yellow, and mixed with a slight excess of oxalic acid. The excess of oxalic acid is then removed by carbonate



of lime, and the filtrate, after being nearly evaporated to dryness, is mixed with alcohol, which precipitates hyposulphate of lime together with a little indigo-yellow, as a brown viscid mass. By evaporating the alcoholic solution, the indigo-yellow is obtained mixed with a little hyposulphate of lime.

Indigo-yellow forms a yellow transparent mass, having neither an alkaline nor an acid reaction.

It swells when heated, evolving an odour of burnt animal matter, and is slowly converted into a combustible charcoal, leaving a slight residue of gypsum.

It is soluble in water and in alcohol, imparting to them a pure yellow colour. The aqueous solution is incompletely precipitated by acetate of lead, but completely by subacetate of lead. The latter precipitate is bright yellow. It is not precipitated by ferric sulphate, sulphate of copper, corrosive sublimate, or infusion of galls.



### Bromisatin.



ERDMANN. (1840.) *J. pr. Chem.* 19, 358; *Pharm. Centr.* 1840, 307.

HOFMANN. *Ann. Pharm.* 53, 40; *Pharm. Centr.* 1845, 294.

#### *Bromisatinase.*

*Formation.* (pp. 42, 52.)

*Preparation.* When fresh indigo-blue is treated with bromine and the yellow mass extracted with boiling water, the filtrate on cooling deposits small quantities of bromisatin, which is purified by crystallisation from alcohol. (Erdmann.) — 2. Powdered isatin, suspended in water, is shaken up, in sunshine, with bromine, which is gradually added, till the liquid, after a fresh addition of bromine, is no longer decolorised on agitation. The compound is then boiled with weak alcohol, freed from hydrobromic acid by washing with water, and recrystallised from boiling alcohol. (Hofmann.)

*Properties.* Small crystals resembling chlorisatin. (Erdmann.) Brilliant prisms. (Hofmann.)

				Hofmann.	Erdmann.
16 C .....	96	...	42.43	..... 42.48	.... 42 to 44.1
N .....	14	...	6.20		
Br .....	80	...	35.41		
4 H.....	4	...	1.78	..... 2.11	
4 O .....	32	...	14.18		♣
<hr/>					
$\text{C}^{16}\text{NBrH}^4\text{O}^4$ ....	226	...	100.00		

Treated with cold potash it yields bromisatate of potash. (Erdmann.) When distilled with hydrate of potash, it behaves like chlorisatin and yields bromaniline.



**Bromisatic Acid.**

Formed by the action of aqueous alkalis upon bromisatin. (Erdmann, Laurent.)

**Bibromisatin.**

ERDMANN. (1840.) *J. pr. Chem.* 19, 360; 24, 8; *Pharm. Centr.* 1840, 308; 1841, 706.

LAURENT. *N. Ann. Chim. Phys.* 8, 380; *Rev. scient.* 10, 302; 18, 458; *Pharm. Centr.* 1842, 248.

HOFMANN. *Ann. Pharm.* 53, 47; *Pharm. Centr.* 1845, 294; *J. pr. Chem.* 35, 109.

*Bromisatinèse.*

*Formation.* (pp. 42, 52.)

*Preparation.* 1. The alcoholic mother-liquor obtained by crystallising bromisatin, contains considerable quantities of bibromisatin. (Erdmann.) — 2. Isatin is treated with bromine as long as vapours of hydrobromic acid continue to be evolved, and the product is crystallised from boiling alcohol. (Laurent.) — 3. Bromine is poured over bromisatin and the whole allowed to digest for a considerable time in sunshine. (Hofmann.)

*Properties.* Orange-yellow, rectangular, four-sided prisms. (Laurent.) It is exactly like bichlorisatin. (Erdmann.)

					Erdmann.	Laurent.	Hofmann.
16 C .....	96	...	31·47	.....	31·80	...	31·77
N .....	14	...	4·59	.....	4·85		
2 Br .....	160	...	52·46				
3 H .....	8	...	0·94	.....	1·12	...	1·16
4 O .....	32	...	10·54				
<hr/>							
C <sup>16</sup> NBr <sup>3</sup> H <sup>3</sup> O <sup>4</sup> .....	305	...	100·00				

When boiled with potash, it forms bibromisatate of potash. (Erdmann.)<sup>a</sup> Melted with hydrate of potash, it forms bibromaniline. (Hofmann.) With alcoholic ammonia it forms bibromimasatin. (Laurent.)

*Bibromisatide of Potassium.* — Bibromisatin dissolves with red colour in cold potash; the solution becomes decolorised after a time, and immediately on heating. (Erdmann.)

When bibromisatin is gently warmed with alcohol and hot alcoholic potash added, a precipitate is formed consisting of black crystalline scales which appear blue by transmitted light. (Laurent.)

When bibromisatin is boiled with alcohol, and ammonia and nitrate of silver are added, a yellow precipitate is formed which turns violet. (Laurent.)

Bibromisatin dissolves readily in alcohol.

### Bibromisatic Acid.\*



ERDMANN. (1839.) *J. pr. Chem.* 19, 360; *Pharm. Centr.* 1840, 308.

*Formation* (p. 70).

*Preparation.* The concentrated aqueous solution of the potash-salt deposits the acid on the addition of hydrochloric acid, as a yellow powder soluble in water. This substance, when dried in vacuo over sulphuric acid is converted, even in the cold, into bibromisatin.

The formula of the *bibromisatates* is  $\text{C}^{16}\text{NBr}^2\text{H}^4\text{MO}^6$ .

The solution of bibromisatate of ammonia, obtained by decomposing bibromisatate of potash with sulphate of ammonia, yields bibromisamate of ammonia on evaporation. (Laurent.)

*Bibromisatate of Potash* is readily obtained in shining straw-coloured needles from the solution of bibromisatin in potash which has become colourless. The salt loses 4.64 per cent. of water (2 atoms) in vacuo at 155°.

			At 100°.	Erdmann.
KO .....	47.2	...	13.07	..... 13.17
16 C .....	96	...	26.58	..... 27.35
N .....	14	...	3.88	
2 Br .....	160	...	44.29	..... 43.79
4 H .....	4	...	1.11	..... 1.50
5 O .....	40	...	11.07	
<hr/>				
$\text{C}^{16}\text{NBr}^2\text{H}^4\text{KO}^6$ .....	361.2	...	100.00	

Bibromisatate of potash dissolves less readily in water and in alcohol than the corresponding salt of bichlorisatic acid.

It forms bright yellow precipitates with chloride of *barium* and chloride of *calcium*. The precipitates dissolve in boiling water, from which they crystallise on cooling.

*Bibromisatate of Lead.* — The potash-salt added to a solution of acetate of lead, precipitates bright yellow flakes, which dissolve in water and crystallise from the solution in reddish-yellow grains.

*Bibromisatate of Copper.* — The potash-salt forms with sulphate of copper a gelatinous precipitate which turns greenish-yellow and flocculent in a few moments, and after a time becomes blood-red and granular.

\* See page 51.

The greenish-yellow precipitate remains unchanged if rapidly thrown upon a filter, washed, and pressed between paper; but turns red when dried in vacuo.

*Bibromisatate of Silver.* — The potash-salt forms with nitrate of silver a yellow granular precipitate which dissolves in boiling water and crystallises out on cooling.

### Bibromisato-sulphurous Acid.

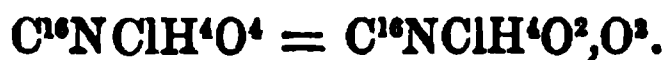


LAURENT. *Rev. scient.* 10, 295; *J. pr. Chem.* 28, 336.

The potash-salt of this acid is formed as a yellow precipitate when sulphurous acid is passed through bibromisatate of potash. It is very sparingly soluble in water. When treated with acids, it evolves sulphurous acid and deposits bibromisatin. The dried salt contains 10.0 per cent. of potash.

### Oxychlorazo-nucleus $C^{16}NClH^4O^2$ .

#### Chlorisatin.



ERDMANN. (1840.) *Ann. Pharm.* 23, 129; *J. pr. Chem.* 19, 317; 22, 270; 24, 5; *Pharm. Centr.* 1840, 112, 296; 1841, 214, 706.

G. ROSE. *J. pr. Chem.* 22, 299.

LAURENT. *N. Ann. Chim. Phys.* 3, 378; *Rev. scient.* 9, 31; 10, 301; 18, 458; 19, 162; *J. pr. Chem.* 35, 108; *Pharm. Centr.* 1842, 247.

HOFMANN. *Ann. Pharm.* 53, 12; *Pharm. Centr.* 1845, 274.

#### Chlorisatinase.

*Formation.* By the action of chlorine upon indigo-blue (Erdmann p. 41), or upon isatin. (Laurent, Hofmann, p. 52.)

*Preparation.* When the pulverulent reddish-yellow mixture of chlorisatin and bichlorisatin, obtained by submitting indigo-blue to the action of chlorine, is dissolved in boiling alcohol, the solution, on cooling, deposits crystals consisting chiefly of chlorisatin, which may be purified from bichlorisatin by recrystallisation. The product is often coloured brown from adhering resin: hence the formation of large crystals must be prevented by stirring the solution. (What becomes of the resin? Gm.) (Erdmann.) — 2. Chlorine is passed through gently warmed water, containing isatin in suspension, till the powder acquires a pure orange-yellow colour.

(Laurent.) The formation of chlorisatin is greatly facilitated by boiling liquid and passing the chlorine through it in sunshine. (Hofmann.) — 3. Chlorisatate of potash is decomposed by hydrochloric acid. (Erdmann.)

*Properties.* Orange-yellow, transparent, four-sided prisms or laminæ (Erdmann); small capillary orange-red crystals, with very brilliant faces. (Fig. 65)  $u : u' = 131^\circ$ ;  $u' : t = 140^\circ 30'$ ;  $i : i = 134^\circ 12'$  (G. Rose);  $u : u' = 131^\circ 132^\circ$ . (Laurent.) Hence it is isomorphous with isatin. It is inodorous, and has a bitter taste; its dust provokes sneezing. The solution imparts an unpleasant smell to the skin. It does not give off any water at  $100^\circ$ , but at a higher temperature, part of it sublimes undecomposed in transparent orange-coloured needles. (Erdmann.)

				Erdmann.	Laurent.
16 C .....	96	...	52.92	53.30	53.11
N .....	14	...	7.72	8.05	
Cl .....	35.4	...	19.51		
4 H .....	4	...	2.21	2.32	2.35
4 O .....	32	...	17.64		
<hr/>					
$C^{16}NClH^4O^4$ .....	181.4	...	100.00		

*Decompositions.* 1. Chlorisatin, when strongly heated, blackens, melts, and decomposes, swelling up considerably, and evolving yellow vapours which smell like those from heated indigo. It burns in the air with a brilliant flame, and leaves a residue of difficultly combustible charcoal, which, when burnt in the flame of a spirit-lamp, imparts to it a green colour. (Erdmann.) — 2. It is not acted upon by *chlorine* in presence of water. When it is dissolved in hot alcohol of 80 per cent. and chlorine gas is passed through the liquid, until only products of the decomposition of alcohol are formed, a brownish-yellow, viscid, oily mass is deposited at the bottom of the vessel, containing shining laminæ of chloranil; water extracts chloride of ammonium from it, and alcohol dissolves chloride of ethyl, quintachlorocarbolic acid, and a resinous mass which forms the largest portion of the product. The supernatant yellow solution contains products of the action of chlorine upon alcohol, and yields by distillation a residue corresponding to the viscid substance, but not containing chloranil. (Erdmann, Hofmann.) *Bromine* does not act upon chlorisatin. (Hofmann.)

3. Warm *nitric acid* dissolves chlorisatin, with violent evolution of nitrous fumes, and forms a yellow solution from which water precipitates a white powder; the precipitate shrinks together when heated. If the action of the nitric acid is prolonged, crystals of oxalic acid and nodular grains of a nitrogen-acid are formed; if the latter are recrystallised from water, they unite together in transparent crystals, which dissolve in potash forming a brown solution. (Erdmann.) When chlorisatin is dissolved in nitric acid, and a few drops of hydrochloric acid are added, a violent action results, and a more thorough decomposition takes place, without formation of bichlorisatin. (Hofmann.) — 4. Chlorisatin dissolves in *sulphuric acid*, imparting to it a dark brown colour, and appears to be precipitated undecomposed from the solution by water. — With *ammonia*, it forms chlorimesatin and chlorimasitin. — 6. *Sulphuretted hydrogen* pro-

duces, in an alcoholic solution of chlorisatin, a white precipitate of sulphochlorisatin (chloroquadrisulphiatyde, according to Gerhardt); sulphide of ammonium forms chlorisatyde. (Erdmann.) Chlorisatin dissolves with dark red colour in an aqueous solution of monosulphide of potassium, and forms an almost opaque solution, which when heated turns yellow and deposits reddish grey flakes containing sulphur. If the filtrate is evaporated after all the sulphide of potassium has become oxidised by exposure to the air, chlorisatate of potash free from sulphur may be extracted by alcohol from the residue. (Erdmann.) — 7. *Potash* dissolves chlorisatin with deep red colour, which gradually becomes bright yellow in the cold (immediately on boiling), while chlorisatate of potash is formed. (Erdmann, Laurent.) On distilling chlorisatin with hydrate of potash, hydrogen is evolved and chloraniline is formed:



when the residue has become nearly solid, ammonia is evolved together with the hydrogen, a blue sublimate is deposited upon the upper part of the retort, and the oily drops which pass over become brown and do not solidify any more on cooling. Chlorisatin intimately mixed with *quicklime* and carefully heated, is completely converted into chloraniline. (Hofmann.)

*Combinations.* Chlorisatin dissolves but slightly in cold water; it requires for its solution 1000 parts of water at  $0^\circ$ , and more than 200 parts of boiling water.

Chlorisatin, like isatin, unites with basic oxides, forming compounds called *chlorisatides*.

*Chlorisatide of Potassium.* — A solution of chlorisatin mixed with caustic potash becomes deep red; but the colour rapidly passes away since chlorisatate of potash is formed. Solid chlorisatin, treated with potash, turns almost black, but gradually dissolves with golden-yellow colour. (Erdmann.)

*Chlorisatide of Silver.* — When nitrate of silver is mixed with alcoholic chlorisatin containing a little ammonia, a violet-coloured gelatinous precipitate is formed, which contains no ammonia. (Laurent.)

*Chlorisatide of Argentammonium.* — When an alcoholic solution of chlorisatin mixed with ammonia is poured into an ammoniacal solution of nitrate of silver, a precipitate is formed of the colour of wine-lees, consisting of microscopic laminæ. It yields with bichloride of platinum an amount of chloroplatinate of ammonium corresponding to 1 atom of ammonia. (Laurent.)

				Laurent.
$C^{16}NClH^2(NH^4)O^4$ .....	197.4	....	64.91	
Ag .....	108	....	35.09	..... 35.00
<hr/>				
$C^{16}NClH^2(NH^4)AgO^4$ .....	305.4	....	100.00	

Chlorisatin dissolves in 220° parts of alcohol of sp. gr. 0.830 at  $14^\circ$ , and more readily in boiling alcohol. (Erdmann.)

## Chlorisatic Acid.\*



ERDMANN. (1839.) *Ann. Pharm.* 33, 129; *J. pr. Chem.* 19, 337; 24, 5; *Pharm. Centr.* 1840, 113, 296; 1841, 706.

LAURENT. *N. Ann. Chim. Phys.* 3, 378.

*Acide chlorisatinasique.*

*Formation.* (p. 52.)

Chlorisatic acid is not known in the free state.

The formula of the chlorisatates is  $\text{C}^{16}\text{NClH}^6\text{MO}^6$ .

The solution of chlorisatate of ammonia, obtained by decomposing chlorisatate of potash with sulphate of ammonia, yields chlorisamate of ammonia on evaporation.

*Chlorisatate of Potash.* — When a sufficiently concentrated solution of chlorisatin is boiled with potash, crystals of chlorisatate of potash separate out on cooling. These are pressed between paper and exposed to the air, in order that the excess of potash may become saturated with carbonic acid; they are then recrystallised from alcohol. If the chlorisatin contains bichlorisatin and resin, these latter remain in the mother-liquor.

Shining, transparent, bright yellow scales, or flattened four-sided needles. It is readily soluble in water, and tastes intensely bitter. It does not give off water at  $160^\circ$ .

					Erdmann.
KO.....	47.2	...	19.87	.....	21.08
16 C .....	96	...	40.40	.....	41.86
N .....	14	...	5.89		
Cl .....	35.4	...	14.90		
5 H .....	5	...	2.10	.....	2.50
5 O .....	40	...	16.84		
<hr/>					
$\text{C}^{16}\text{NClH}^6\text{KO}^6$ .....	237.6	...	100.00		

It decomposes when heated, with some violence, and leaves a slag-like residue of chloride of calcium mixed with charcoal. — The aqueous solution forms, with hydrochloric acid, a yellow precipitate which immediately redissolves with orange-yellow colour; the solution becomes turbid and deposits crystals of chlorisatin. — It is readily soluble in water, and less soluble in alcohol the more concentrated the spirit; it dissolves in boiling alcohol more abundantly than in cold alcohol.

*Chlorisatate of Baryta.* — A warm aqueous solution of the potash-salt, mixed with chloride of barium, yields, on cooling, sometimes pale needles united in tufts, sometimes deep golden-yellow brilliant laminæ, and often both forms at once; they may be converted into one another by dissolving and crystallising. The light yellow needles give off 1 atom of water at  $160^\circ$ ; the golden-yellow salt, 3 atoms. A solution of chlorisatin in boiling baryta-water deposits, on cooling, crystalline grains united in masses like cauliflower heads. (Erdmann.)

\* See page 54.

At 100°.				Erdmann.
BaO .....	76.6	....	28.69	..... 28.82
16 C .....	96	....	35.95	..... 36.21
N .....	14	....	5.24	
Cl .....	35.4	....	13.26	..... 13.86
5 H .....	5	....	1.88	..... 2.06
5 O .....	40	....	14.98	
<hr/>				
$C^{16}NClH^5BaO^6$ .....	267	....	100.00	

Light yellow needles.				Erdmann.
$C^{16}NClH^5BaO^6$ .....	267	....	96.73	
HO .....	9	....	3.27	..... 3.18
<hr/>				
$C^{16}NClH^5BaO^6 + Aq$ ....	276	....	100.00	

Golden yellow laminae.				Erdmann.
$C^{16}NClH^5BaO^6$ .....	267	....	90.87	
3 HO .....	27	....	9.13	..... 10.45
<hr/>				
$C^{16}NClH^5BaO^6 + 3Aq$ ....	294	....	100.00	

Chlorisatate of potash forms a yellow crystalline salt with *chloride of calcium*.

The potash-salt does not precipitate solutions of sulphate of magnesia, alum, or ferrous sulphate; it forms orange-yellow flakes with nitrate of bismuth, and yellow precipitates with sulphate of zinc and chloride of cadmium.

*Chlorisatate of Lead.* — The potash-salt forms with acetate or nitrate of lead, a shining, yellow, gelatinous precipitate, which in a few minutes (more rapidly when shaken) becomes scarlet-coloured and crystalline. Under the microscope, the yellow amorphous powder may be seen to change into dendrites, or into large crystalline grains. The red precipitate dissolves in boiling water, and red crystalline grains separate out on cooling. At 160° it gives off 5.7 per cent. of water (2 atoms), and assumes a dirty brick-red colour.

				Erdmann.
PbO .....	111.8	....	34.92	..... 37.11
16 C .....	96	....	30.00	..... 31.26
N .....	14	....	4.36	..... 4.26
Cl .....	35.4	....	11.05	
7 H .....	7	....	2.18	..... 2.32
7 O .....	56	....	17.49	
<hr/>				
$C^{16}NClH^5PbO^6 + 2Aq$ .....	320.2	....	100.00	

The potash-salt forms a reddish-brown precipitate with potassio-ferric sulphate; and with chloride or sulphate of *nickel*, a yellow crystalline precipitate after a time. With sulphate or nitrate of *copper*, it forms at first a bulky yellowish red precipitate, which, however, suddenly

turns blood-red, and is deposited as a heavy crystalline powder; if acetate of copper is used, this change takes place very slowly. Acetate of copper gives no precipitate with a very dilute solution of the potash-salt; but if the mixture is then warmed, brown flakes separate out, which require a long time to become red and granular. The potash-salt forms, with mercurous nitrate, a bright yellow precipitate; with mercuric nitrate, a dark yellow precipitate; and with corrosive sublimate, a slight crystalline precipitate, after the mixture has stood for a long time.

*Chlorisatate of Silver.* — The potash-salt forms, with nitrate of silver, a pale yellow precipitate, which dissolves in boiling water, and crystallises, on cooling, in yellowish needles grouped in tufts, or in arborescent ramifications.

				Erdmann.	Laurent.
AgO	116	...	37.86	38.48	37.54
16 C	96	...	31.33	32.35	
N	14	...	4.57		
Cl	35.4	...	11.55		
5 H	5	...	1.63	1.76	
5 O	40	...	13.06		
<hr/>					
$C^{16}NClH^5AgO^6$	306.4	...	100.00		

### Chlorisatosulphurous Acid.



LAURENT. (1842.) *Compt. rend.* 14, 490; *J. pr. Chem.* 26, 123; *Rev. scient.* 10, 294; *J. pr. Chem.* 28, 348.

This acid is not known in the free state.

Chlorisatosulphite of potash is obtained by passing sulphurous acid gas through an aqueous solution of chlorisatate of potash; on evaporating the solution, it separates out as a straw-coloured, scaly, fibrous salt, and is but slightly soluble in water.

				Laurent.
KO	47.2	...	15.65	16.0
$C^{16}NClH^5O^6$	190.4	...	63.13	
2 SO <sup>2</sup>	64	...	21.22	22.0
<hr/>				
$C^{16}NClH^5KO^6, 2SO^2$	301.6	...	100.00	

Yields sulphuric acid when acted upon by chlorine.

Gives, with nitrate of silver, a yellow precipitate, which appears to be a mixture of sulphite of silver and chlorisatin. Ammoniacal nitrate of silver forms a carmine-red precipitate.



*Oxychlorazo-nucleus*  $C^{16}NCl^3H^3O^3$ .**Bichlorisatin.**

ERDMANN. (1840.) *Ann. Pharm.* 23, 129; *J. pr. Chem.* 19, 346; 22, 270; 24, 7; *Pharm. Centr.* 1840, 113, 296; 1841, 214, 706.

LAURENT. *N. Ann. Chim. Phys.* 3, 380; *Rev. scient.* 18, 458; *J. pr. Chem.* 35, 109; *Pharm. Centr.* 1842, 247.

*Formation.* By the action of chlorine gas upon indigo-blue (p. 41).

*Preparation.* When the alcoholic mother-liquor obtained in the preparation of chlorisatin, from which the chlorisatin has been crystallised, (p. 72) is distilled, a mixture of chlorisatin and bichlorisatin first separates out, the latter being obtained purer at each successive crystallisation. The bichlorisatin is purified by recrystallisation from alcohol, or converted into bichlorisatate of potash, and then precipitated from the salt.

*Properties.* Bichlorisatin crystallises from alcohol in small rose-coloured needles or laminæ, and sometimes in four-sided prisms; on the cooling of the alcoholic solution it forms a yellowish-red granular powder. It is distinguished from chlorisatin only by its greater solubility in alcohol, and by the behaviour of the bichlorisatate of lead prepared from it. It sublimes partly undecomposed when heated in a glass tube. Does not give off any water at  $160^\circ$ .

					Erdmann.	Laurent.
16 C	.....	96	....	44.49	.... 44.66	.... 45.59
N	.....	14	....	6.49	..... 6.89	
2 Cl	.....	70.8	....	32.80		
3 H	.....	3	....	1.89	..... 1.57	.... 1.55
4 O	.....	32	....	14.83		
<hr/>						
$C^{16}NCl^3H^3O^4$	.....	215.8	....	100.00		

The bichlorisatin analysed by Laurent still contained chlorisatin.

*Decompositions.* When bichlorisatin is heated in a glass-tube, the unsublimed portion melts and forms a black carbonaceous mass. It burns when heated in the air, and leaves a residue of charcoal which tinges the edges of a spirit-flame with green. — 2. When it is suspended in water and a stream of chlorine is passed through the liquid, it is not decomposed, even in sunshine. The alcoholic solution gives the same products of decomposition as chlorisatin (p. 73). — 3. With nitric acid it behaves like chlorisatin; but even when it is boiled with concentrated acid, a part remains undissolved and resembles unchanged bichlorisatin,—dissolving readily in potash and being precipitated from the solution by hydrochloric acid as a bright-yellow powder, upon which boiling water has no action. On prolonged boiling and evaporation with

nitric acid, a nitrogenised substance is formed similar to that in the case of chlorisatin; the former is however more soluble, crystallises less easily, and separates, as the hot aqueous solution cools, in indistinctly crystalline flakes. — 4. Heated with aqueous *potash*, it forms bichlorisatate of potash. (Erdmann.) — Distilled with hydrate of potash, it yields bichloraniline. (Hofmann.) — 5. With *ammonia*, it behaves like chlorisatin. — 6. With *sulphide of potassium* it undergoes the same decompositions as chlorisatin, and yields bichlorisatate of potash. (Erdmann.)

**Combinations.** Bichlorisatin dissolves in water rather more readily than chlorisatin, and imparts to it a darker colour. (Erdmann.)

**Bichlorisatide of Potassium.** — When hydrate of potash is moistened with absolute alcohol and gently heated with bichlorisatin, a red solution is formed, which in a few seconds solidifies into a violet-black paste of bichlorisatide of potassium. The solution produces a violet-coloured precipitate with silver-salts.

Bichlorisatin dissolves in cold aqueous potash with a deep red colour which changes to pale yellow on heating. (Erdmann.)

Bichlorisatin dissolves at 14° in 30 parts of alcohol of sp. gr. 0·83. (Erdmann.)

## Bichlorisatic Acid.



ERDMANN. (1839.) *Ann. Pharm.* 88, 129; *J. pr. Chem.* 19, 846; 24, 7; *Pharm. Centr.* 1840, 116, 296; 1841, 706.

LAURENT. *N. Ann. Chim. Phys.* 3, 378.

**Formation** (p. 78).

**Preparation.** Bichlorisatic acid is precipitated from the concentrated solution of its potash-salt, on the addition of hydrochloric, sulphuric, nitric, oxalic, or tartaric acids, as a yellow powder, which must be pressed between folds of blotting paper. (Acetic acid does not precipitate bichlorisatic acid.) When the acid is separated from the lead-salt by sulphuretted hydrogen and the filtered solution evaporated in vacuo, a flaky crystalline mass is obtained, which is coloured yellowish red at the edges, owing to the formation of a little bichlorisatin.

**Properties.** Bichlorisatic acid is a bright yellow powder.

**Decompositions.** After drying in vacuo, it gives off 7·24 to 8·17 per cent. of water (2 atoms) at 100°, and is converted into bichlorisatin. (Theory requires 7·70 per cent.) The aqueous solution, heated to 60°, turns reddish yellow, becomes turbid, and deposits bichlorisatin.

**Combinations.** The acid dissolves readily in cold water, communicating to it a bright yellow colour.

The formula of the *bichlorisatates* is  $C^{16}NCl^2H^4MO^6$ .

The solution of bichlorisatate of ammonia, obtained by decomposing bichlorisatate of potash with sulphate of ammonia, yields bichlorisamide on evaporation. (Laurent.)

*Bichlorisatate of Potash.* — When bichlorisatin is dissolved in aqueous potash, the solution becomes pale yellow on heating; and if then allowed to cool, deposits pale yellow crystalline scales, which cause the whole mass to solidify. These crystals are purified by pressing and repeated crystallisation from strong alcohol. Bichlorisatate of potash, after being dried at  $130^\circ$  in vacuo, gives off 6.29 per cent. of water (2 atoms ?) at  $160^\circ$ , and when crystallised from alcohol only 4.3 per cent. (1 atom ?).

				Erdmann.
KO .....	47.2	...	17.35	17.10
16 C .....	96	...	35.29	36.09
N .....	14	...	5.15	5.33
2 Cl .....	70.8	...	26.04	26.65
4 H .....	4	...	1.47	1.83
5 O .....	40	...	14.70	13.00
<hr/>				
$C^{16}NCl^2H^4KO^6$ ...	272.0	...	100.00	100.00

It blackens when heated, and then suddenly decomposes, at the same time glowing and emitting a yellow smoke, and leaves a scoriated residue of carbon, which burns when heated in the air, leaving chloride of potassium with a trace of carbonate of potash.

It is readily soluble in cold water and still more in boiling water, so that the boiling solution solidifies into a mass of pearly laminæ.

It dissolves with difficulty in cold alcohol, but more easily in boiling alcohol, and more abundantly the weaker the spirit.

*Bichlorisatate of Baryta.* — The solution of the potash-salt mixed with chloride of barium and allowed to stand for some time after cooling, deposits shining golden yellow needles and laminæ. On mixing the cold solutions, the salt is obtained as a yellow powder. It loses 2 atoms of water at  $160^\circ$ .

				Erdmann.
At $160^\circ$ .				
BaO .....	76.6	...	25.41	25.73
16 C .....	96	...	31.85	32.50
N .....	14	...	4.64	5.09
2 Cl .....	70.8	...	23.49	23.83
4 H .....	4	...	1.33	1.72
5 O .....	40	...	13.28	11.13
<hr/>				
$C^{16}NCl^2H^4BaO^6$ .....	301.4	...	100.00	100.00

				Erdmann.
Crystallised.				
$C^{16}NCl^2H^4BaO^6$ .....	301.4	...	94.37	
2 HO .....	18	...	5.63	5.73
<hr/>				
$C^{16}NCl^2H^4BaO^6 + 2Aq$ .....	319.4	...	100.00	

The potash-salt does not precipitate sulphate of magnesia, alum, chrome-alum or sulphate of manganese.

The potash-salt precipitates nitrate of bismuth in orange-coloured flakes and gives *with lead-salts* a yellow precipitate, the colour of which does not change; it precipitates iron-alum brownish red, and nitrate of manganese bluish-green.

*Bichlorisatate of Copper.* — The potash-salt forms with sulphate or nitrate of copper, a precipitate which is at first voluminous and of the colour of hydrated sesquioxide of iron; but it rapidly becomes flocculent and of a pale greenish yellow colour, and is finally precipitated as a beautiful carmine-red, heavy granular powder. The greenish yellow precipitate consists of microscopic, capillary, transparent crystals, which, when the colour changes to red, are converted into separate grains. The potash-salt forms with acetate of copper a brown precipitate, which becomes red after a long time only, and without previously turning greenish yellow. The dried salt is carmine-red and takes a golden lustre when burnished. It gives off a little water at 150°.

					Erdmann.
CuO.....	40	...	15.11	.....	15.25
16 C .....	96	...	36.25	.....	37.34
N .....	14	...	5.28	.....	5.42
2 Cl .....	70.8	...	26.74	.....	26.60
4 H .....	4	...	1.51	.....	1.94
5 O .....	40	...	15.11	.....	13.45
<hr/>					
C <sup>16</sup> NCl <sup>2</sup> H <sup>4</sup> CuO <sup>6</sup> ...	264.8	...	100.00	.....	100.00

The potash-salt forms yellow precipitates with mercurous and mercuric nitrates, but does not precipitate a solution of corrosive sublimate.

The potash-salt gives with nitrate of silver a yellow precipitate which dissolves in a large quantity of boiling water and crystallises out on cooling in small, yellowish, transparent needles united in the form of tufts.

When heated in the air, it melts into a brown mass, from which bichlorisatin sublimes, and leaves a residue of metallic silver, carbon, and a little chloride of silver. It contains from 33 to 35.4 per cent. of oxide of silver. The formula C<sup>16</sup>NCl<sup>2</sup>H<sup>4</sup>AgO<sup>6</sup> requires 34.04 per cent.

### Bichlorisatosulphurous Acid.



LAURENT. *Rev. scient.* 10, 294.

When bichlorisatin is boiled with bisulphite of potash, small yellowish needles of bichlorisatosulphite of potash are obtained, which are decomposed by acids into bichlorisatic and sulphurous acids. The salt is slightly soluble in cold water.

					Laurent.
KO .....	47.2	...	14.09	.....	14.2
C <sup>16</sup> NCl <sup>2</sup> H <sup>4</sup> O <sup>5</sup> , 2SO <sup>3</sup> .....	288.8	...	85.91		
<hr/>					
C <sup>16</sup> NCl <sup>2</sup> H <sup>4</sup> KO <sup>6</sup> , 2SO <sup>3</sup> .....	336.0	...	100.00		

*Oxyamidazo-nucleus*  $C^{16}NAdH^4O^2$ .**Imesatin.**

LAURENT. (1841.) *N. Ann. Chim. Phys.* 3, 484; *J. pr. Chem.* 25, 457;  
*Pharm. Centr.* 1842, 260; *Rev. scient.* 18, 472; *J. pr. Chem.* 85, 121.

*Formation.* By the action of gaseous ammonia on an alcoholic solution of isatin:



*Preparation.* 1. Boiling absolute alcohol is saturated with isatin, and a little more powdered isatin is added; dry gaseous ammonia is then passed through the hot solution, whereupon the powdered isatin soon dissolves. The solution saturated with gaseous ammonia deposits in 6 — 24 hours beautiful brownish yellow crystals. They are often mixed with a crystalline powder consisting of isatimide: hence it is advisable to pour off the solution from the large crystals, before any pulverulent isatimide has separated out; the latter may also be separated by washing the crystals with alcohol, or by treating them with boiling alcohol, in which the imesatin is more soluble. — 2. A more certain method of obtaining pure imesatin is to pass gaseous ammonia through ether containing isatin in suspension; the ether should be gently warmed at first. Imesatin crystallises out on evaporation.

*Properties.* Imesatin forms dark yellow, straight, rectangular prisms without truncation-faces. It is inodorous.

					Laurent.
16 C .....	96	...	65.75	.....	65.24
2 N .....	28	...	19.17	.....	19.21
6 H .....	6	...	4.11	.....	4.27
2 O .....	16	...	10.97	.....	11.28
<hr/>					
$C^{16}N^2H^6O^2$ .....	146	...	100.00	.....	100.00 ●

*Decompositions.* Imesatin when heated melts, froths up and evolves ammonia, whilst white cubical laminæ and a reddish brown and partly crystalline mass sublime, leaving a large residue of charcoal. — It dissolves in potash with brownish red colour; ammonia is evolved on heating, and if the solution be then neutralised with an acid, isatin is precipitated. — It is readily dissolved on warming it with a mixture of alcohol and hydrochloric acid; the liquid yields crystals of isatin on cooling, and contains chloride of ammonium in solution.

Imesatin is insoluble in water.

It dissolves pretty readily in boiling *alcohol*, but is insoluble in ether.

## Phenylimesatin.



ENGELHARDT. (1855.) *Bull. de Petersb.* 13, 357; *J. pr. Chem.* 65, 261; *Pharm. Centr.* 1855, 356.

**Formation.** By the action of aniline on isatin dissolved in absolute alcohol.

**Preparation.** 7.35 parts of isatin are dissolved in a little absolute alcohol and 4.35 parts of aniline added: the whole is then heated to boiling. On cooling, 10.5 parts of phenyl-imesatin crystallise out, and may be purified by recrystallisation from alcohol.

**Properties.** Small, yellow, transparent, needle-shaped prisms, which are united in the form of stars and sharply pointed.

				Engelhardt.
28 C .....	168	...	75.67	76.04
2 N .....	28	...	12.61	12.96
10 H .....	10	...	4.51	5.09
2 O .....	16	...	7.21	5.91
<hr/>				
$\text{C}^{28}\text{N}^2\text{H}^{10}\text{O}^2$ .....	222	...	100.00	100.00

**Decompositions.** When phenylimesatin is heated on platinum foil, it at first melts into a dark red liquid, which solidifies into an amorphous mass; when more strongly heated, it decomposes, evolves yellow vapours which attack the organs of respiration, and leaves a large residue of carbon. — Heated with *nitric acid*, it dissolves with red colour and without evolution of red fumes. It forms with *strong sulphuric acid* a dark red solution which becomes yellow on diluting with water. — It becomes dark red on warming with potash and yields vapours of aniline and a solution of isatate of potash. — The alcoholic solution of phenylimesatin, mixed with a little hydrochloric acid and boiled, turns red and yields crystals of isatin on cooling, while chloride of aniline remains in solution. It dissolves very slightly in boiling water; and the solution on cooling deposits flakes consisting of very fine golden-yellow needles.

It dissolves readily in boiling *alcohol*, much less readily in cold alcohol.

It is soluble in *ether*.

## Bromophenylimesatin.



ENGELHARDT. (1855.) *Bulletin de Petersb.* 13, 379; *J. pr. Chem.* 65, 266; *Pharm. Centr.* 1855, 461.

**Formation.** By the action of bromaniline on isatin.

## 84 PRIMARY NUCLEUS $C^{16}H^3$ : OXYAMIDAZO-NUCLEUS $C^{16}NAdH^4O^2$ .

*Preparation.* 3.15 parts of isatin are dissolved in a little boiling alcohol of 80 per cent. and 3.68 parts of bromaniline are added; the whole is then heated to boiling. On cooling, the solution solidifies into a crystalline mass, which is purified by washing with weak alcohol and recrystallisation. 5.68 parts of bromophenylimesatin are obtained.

*Properties.* Fine, flexible, orange-yellow needles having a silky lustre.

				Engelhardt.
28 C .....	168	...	55.81	..... 56.45
2 N .....	28	...	9.30	
Br.....	80	...	26.58	
9 H .....	9	...	2.99	..... 3.50
2 O .....	16	...	5.32	
<hr/>				
$C^{28}N^2Br^1HO^2$ .....	301	...	100.00	

*Decompositions.* When bromophenylimesatin is heated on platinum-foil it melts, decomposes and leaves a residue of charcoal. — Heated with hydrochloric acid, it forms a red solution which deposits crystals of isatin, and if the mother-liquor is diluted with water and potash added, a white precipitate of bromaniline is formed. — The alcoholic solution boiled with hydrochloric acid, yields isatin and hydrochlorate of bromaniline. — Heated with potash, it first turns red, then dissolves and deposits bromaniline, while a yellow solution of isatate of potash is formed.

It is almost insoluble in water. Dissolves readily in boiling alcohol, but much less readily in cold alcohol.

### Chlorophenylimesatin.



ENGELHARDT. *J. pr. Chem.* 65, 266.

Prepared from 2.325 parts of isatin and 2.012 parts of chloraniline, in a similar manner to bromophenylimesatin. 3.129 parts of chlorophenylimesatin are obtained.

Orange-yellow capillary needles.

				Engelhardt.
28 C .....	168	...	65.50	..... 66.05
2 N .....	28	...	10.91	
Cl .....	35.4	...	13.84	
9 H .....	9	...	3.51	..... 3.73
2 O ... ..	16	...	6.24	
<hr/>				
$C^{28}N^2ClH^3O^2$ .....	256.4	...	100.00	

When warmed with hydrochloric acid or potash, it behaves in a similar manner to bromophenylimesatin.

It is insoluble in water, readily soluble in boiling alcohol, and slightly in cold alcohol.

*Oxychloramidazo-nucleus*,  $C^{16}NAdClH^3O^3$ .

### Chlorimesatin.



LAURENT. (1841.) *N. Ann. Chim. Phys.* 3, 494; *J. pr. Chem.* 25, 457; *Pharm. Centr.* 1842, 263.

#### *Imechlorisatinase.*

*Formation.* By the action of dry gaseous ammonia on an alcoholic solution of chlorisatin.

*Preparation.* When dry gaseous ammonia is passed into a solution of chlorisatin in absolute alcohol, a yellow crystalline deposit is formed which may be washed with alcohol.

*Properties.* Brilliant yellow six-sided laminæ.

					Laurent.
16 C .....	96	...	53.21	.....	52.9
2 N .....	28	...	15.52	.....	15.6
Cl .....	35.4	...	19.62		
5 H .....	5	...	2.77	.....	2.8
2 O .....	16	...	8.88		
<hr/>					
$C^{16}N^2ClH^5O^3$ .....	180.4	...	100.00		

*Decompositions.* When heated, it gives off ammonia, and yields a yellow sublimate consisting of fine crystalline needles. — Dissolves in boiling water with evolution of ammonia. Forms chloride of ammonium with dilute hydrochloric acid; dissolves in potash, forming a red solution which, when boiled, evolves ammonia, turns yellow, and then yields chlorisatin on being treated with an acid.

Dissolves very sparingly in boiling alcohol and not at all in ether.

*Compounds containing two or more atoms of  $C^{16}NH^5O^3$ , or similar nuclei.*

### Indin.



LAURENT. (1841.) *Compt. rend.* 12, 539; *N. Ann. Chim. Phys.* 3, 471; *J. pr. Chem.* 25, 455; *Pharm. Centr.* 1842, 251; *Compt. chim.* 1849, 196; *J. pr. Chem.* 47, 159.

*Formation.* By the action of potash on isatyde (p. 98), or sulphisatyde (p. 103); by heating isatan (p. 97).

\* = 2 Atoms of Indigo-blue.



*Preparation.* Bisulphisatyde is placed in a mortar and potash poured upon it so that a stiff magma is formed, which is rubbed up for some time, and potash added drop by drop. When, after 5 or 6 minutes, the mass turns rose-coloured, alcohol is gradually added and the whole is constantly stirred, until a dark rose-coloured paste is formed which is diluted with alcohol and filtered, and the residue is first washed with alcohol and then with water. Since the indin thus obtained contains abundance of sulphisatyde, the water is removed from it by washing with alcohol, which is allowed to run through the filter; and the indin is then taken from the filter and treated with very strong lukewarm potash, wherein it immediately forms a black solution, which after a few hours solidifies into a magma of black needles of indin-potassium. (If the potash is too hot, the black colour disappears, and the indin is completely destroyed.) It is then diluted with absolute alcohol and the solution removed with a pipette; and the crystals are washed on a small filter with common alcohol, then with dilute hydrochloric acid, and finally with water, whereby they are gradually reduced to red pulverulent indin. To obtain indin crystallised, the black crystals are dissolved in boiling absolute alcohol, and the boiling solution is mixed with hydrochloric acid: microscopic crystals then separate out on cooling.

*Properties.* Dark rose-coloured powder or fine microscopic needles. Neutral to test-papers.

						Laurent.			
						a.	b.	c.	
32 C .....	192	....	73.28	....	71.58	.....	72.90	....	71.8
2 N .....	28	....	10.68	....	11.00				
10 H .....	10	....	3.82	....	4.62	.....	3.88	....	4.2
4 O .....	32	....	12.22	....	12.80				
<hr/>									
C <sup>32</sup> N <sup>2</sup> H <sup>10</sup> O <sup>4</sup> .....	262	....	100.00	....	100.00				

Isomeric with indigo-blue. — The analysis *a* was made at an earlier date; *c* probably contained hydrindin. (Laurent.)

*Decompositions.* 1. Indin swells up when heated, and as soon as it melts, yields a sublimate consisting of crystalline needles, and leaves a large residue of charcoal. — 2. It yields nitrindin on boiling with nitric acid. — 3. With bromine it forms bibromindin. — 4. It is decomposed by potash, forming various products. Ammonia does not act upon it. — 5. Boiled with bisulphite of ammonia, it forms a compound which, when boiled with hydrochloric acid, does not give off sulphurous acid or yield any precipitate of indin; this compound forms, with nitrate of silver, a yellow precipitate, which on boiling turns reddish, afterwards black, and then contains sulphide of silver. (*Rev. scient.* 10, 299.)

*Combinations.* Indin is insoluble in water. It dissolves with red colour in sulphuric acid, from which it is precipitated unchanged by water.

*Indin-potassium.* — When indin is moistened with a little alcohol, warmed, and strong alcoholic potash added, it is quickly dissolved; and the black solution, if immediately taken from the fire, deposits small black crystals. The solution must be removed by decantation, and the crystals rapidly washed with absolute alcohol, then laid upon paper and

dried in vacuo on a porous tile. It must be immediately analysed, since the crystals rapidly attract moisture from the air, decomposing into potash and indin. It contains from 11.5 to 12.0 per cent. of potassium, and corresponds to the formula  $C^{32}N^2H^9KO^4$  (theory requires 13.0 per cent.) (Laurent.) [The formula  $C^{32}N^2H^{11}KO^6$  requires 12.3 per cent. potassium; according to this, the crystals would be the potash-salt of an acid bearing the same relation to indin that isatic acid bears to isatin, L.]

Indin is very slightly soluble in boiling alcohol and ether.

### Bibromindin.



ERDMANN. (1841.) *J. pr. Chem.* 22, 265; *Pharm. Centr.* 1840, 212.

LAURENT. *N. Ann. Chim. Phys.* 3, 371; *J. pr. Chem.* 25, 445.

*Formation.* 1. By the action of bromine on indin. (Laurent.) — 2. By heating bibromisatyde. (Erdmann.) — 3. By the action of bromine upon bisulphisatyde. (Laurent.)

*Preparation.* Indin is treated with bromine, whereupon hydrobromic acid is evolved and a violet-black powder is formed. (Laurent.) — 2. Bibromisatyde is heated to a temperature not exceeding  $220^{\circ}$ , and bibromisatin and undecomposed bibromisatyde are removed from the product by treating it with boiling alcohol. (Erdmann.) — 3. Bromine is poured upon bisulphisatyde, whereupon hydrobromic acid and bromide of sulphur are evolved, and the soft brown mass thus formed is treated with ether, which extracts resin and an orange-yellow crystalline mass, leaving bibromindin in the form of a violet-black powder. (Laurent.)

*Properties.* Prepared according to 1 and 3, it is a violet-black powder; prepared according to 2, it is blackish red.

*Decompositions.* 1. When bibromindin is heated between two platinum covers, the greater part chars. Placed on glowing charcoal, it yields a sublimate of shining copper-coloured laminæ, which appear violet by transmitted light under the microscope. (Laurent.) — 2. It blackens when treated with potash; if water is added and the whole boiled, the bibromindin gradually dissolves and forms a yellow solution, from which acids precipitate yellow flakes. When it is boiled with alcohol and solid hydrate of potash, a blackish red solution is formed from which water or hydrochloric acid precipitates violet-coloured bibromindin. (Laurent.)

It is slightly soluble in alcohol (Erdmann, Laurent), and in ether. (Laurent.)

### Chlorindin.



ERDMANN. *J. pr. Chem.* 22, 264; *Pharm. Centr.* 1841, 211.

*Formation.* From chlorisatyde, by the action of heat, or by treating it with potash.

*Preparation.* 1. Chlorisatyde is heated to  $200^{\circ}$ , and the product is freed from chlorisatin and undecomposed chlorisatyde by boiling alcohol. — 2. Chlorisatyde is dissolved in warm potash, and allowed to cool; and the mother-liquor is poured off from the deposit of chlorisatate of potash and mixed with acetic acid, which precipitates yellow chlorisatic acid. On subsequently heating the filtrate with hydrochloric acid, it assumes a deep orange colour and deposits violet flakes of chlorindin, which are filtered from the hot solution.

*Properties.* Chlorindin forms a dirty violet powder, insoluble in water and in hydrochloric acid.

					Erdmann.	
					(1)	(2)
32 C	.....	192	....	58.04	.....	57.04 .... 57.43
2 N	.....	28	....	8.46		
2 Cl	.....	70.8	....	21.40	.....	22.34
8 H	.....	8	....	2.43	.....	2.78 .... 2.70
4 O	.....	32	....	9.67		
$C^{32}N^2Cl^2H^8O^4$ .....					330.8	.... 100.00

It dissolves in potash and forms a yellowish solution with which hydrochloric acid gives a yellow precipitate, soluble with yellow colour in water.

Chlorindin is insoluble in alcohol.

### Bichlorindin.



ERDMANN. *J. pr. Chem.* 22, 264.

Produced from bichlorisatyde : 1. By the action of heat below  $200^{\circ}$ ; 2. By the action of potash (p. 102).

*Preparation.* Bichlorisatyde is heated to  $200^{\circ}$ , and chlorisatin and undecomposed bichlorisatyde are extracted from the product by boiling alcohol. — 2. Bichlorisatyde is dissolved in warm potash and allowed to cool, the precipitate of bichlorisatate of potash is filtered off, and the filtrate mixed with hydrochloric acid. The dirty yellow precipitate thus formed is boiled with water and then with alcohol, which dissolves bichlorisatic acid and leaves violet-coloured bichlorindin undissolved.

*Properties.* Exactly like chlorindin.

### Nitrindin.



LAURENT. (1841.) *N. Ann. Chim. Phys.* 3, 478; *J. pr. Chem.* 25, 452; *Pharm. Centr.* 1842, 258; *Compt. chim.* 1849, 198; *J. pr. Chem.* 47, 161.

*Formation.* By boiling indin or hydrindin with nitric acid. Isatyde

and sulphasatyde probably also yield nitrindin when boiled with nitric acid.

*Preparation.* Indin boiled with nitric acid, is converted into a violet powder, with evolution of red vapours. If the boiling is continued too long, the powder redissolves and water precipitates only a small quantity of yellow matter from the yellow solution. The product is washed with water, and then with boiling alcohol and ether, by which a small quantity of a yellow substance is extracted.

*Properties.* Bright violet powder.

					Laurent.			
					a.	b.		
32 C	.....	192	....	54.54	.....	52.14	....	54.1
4 N	.....	56	....	15.91	.....	15.50	....	15.5
8 H	.....	8	....	2.27	.....	2.52	....	2.5
12 O	.....	96	....	27.28	.....	29.84	....	27.9
<hr/>								
C <sup>32</sup> N <sup>4</sup> H <sup>8</sup> O <sup>12</sup>	.....	352	....	100.00	.....	100.00	....	100.0

*Decompositions.* 1. Nitrindin decomposes pretty rapidly when heated in closed vessels, and leaves a residue of bulky charcoal, which glows even out of contact with the air. — 2. It is gradually decomposed by boiling nitric acid. — 3. It dissolves in potash, forming a deep brown solution, from which hydrochloric acid sometimes throws down undecomposed indin and sometimes yellow flakes, especially if the solution has been boiled. — 4. With sulphite of ammonia it behaves like indin. — Ammonia is without action upon it.

Nitrindin is insoluble in water, and but very slightly soluble in alcohol and in ether.

## Hydrindin.



LAURENT. (1841.) *N. Ann. Chim. Phys.* 3, 475; *J. pr. Chem.* 25 449; *Pharm. Centr.* 1842, 257; *Compt. Chim.* 1849, 199; *J. pr. Chem.* 47, 162.\*

*Formation.* By the action of alcoholic potash upon indin, isatan, isatyde, sulphisatyde, and bisulphisatyde.

*Preparation.* 1. Indin moistened with alcohol is warmed with strong potash, until the solution, which is at first black, has become colourless; and the crystals of hydrindin-potash, which separate out on cooling, are completely freed from potash by water. — 2. When isatyde is treated with potash and a little alcohol, a beautiful rose-coloured solution is formed, which, when mixed with hydrochloric acid and gently evaporated, becomes yellow, and deposits on cooling a mixture of isatin and hydrindin, from which the isatin is extracted by treating with a little

\* = 2 Atoms of Indin + 2HO.

boiling alcohol. Sometimes when indin is treated with alcoholic potash black crystals of indin-potash separate out. (See also p. 99.)— 3. Sulphisathyde dissolves completely in gently heated potash, and on cooling, hydrindin-potash sometimes separates out in beautiful, small, pale yellow crystals; sometimes, however, the solution solidifies into a mass of needles having a silky lustre. The whole is mixed with a large quantity of water, and the crystals are washed on a filter till all the potash is extracted. The filtrate mixed with hydrochloric acid still deposits a small quantity of hydrindin, together with a substance which is perhaps indin.

*Properties.* Hydrindin forms a white or pale yellow powder. When dissolved in boiling alcohol, it separates from the solution on cooling in small rhombic or six-sided needles.

I.		Laurent.	
64 C	384	70.85	
4 N	56	10.33	
22 H	22	4.06	
10 O	80	14.76	
<hr/> $C^{64}N^4H^{22}O^{10}$		542	100.00

II.		Laurent.	
64 C	384	70.59	69.80
4 N	56	10.29	10.70
24 H	24	4.41	4.85
10 O	80	14.71	14.65
<hr/> $C^{64}N^4H^{22}O^{10} + 2Aq$		544	100.00

Gerhardt (*Traité* III, 619) prefers the calculation No. II, since, according to Laurent's formula I, the analysis gives too much hydrogen; this opinion, however, is not in accordance with the analysis of the potash-compound. According to II, hydrindin = 2 At. Indin + 2H. (L.)

*Decompositions.* When hydrindin is carefully heated above  $300^{\circ}$ , it turns violet-brown and gives off 4 atoms of water; the residue behaves with alcoholic potash like indin. — 2. With boiling nitric acid it forms a violet powder, similar to nitrindin.

*Combinations.* It is insoluble in water.

*Hydrindin potash.* — When hydrindin is dissolved in warm potash, this salt separates out on cooling in beautiful, short, brilliant, pale yellow prisms, or in silky needles. If to the solution of the prisms in boiling alcohol containing a little potash, a small quantity of water is added, the whole solidifies on cooling into a magma of crystalline silky needles. A larger quantity of water removes all the potash.

I.			
64 C	384	60.54	
4 N	56	8.83	
27 H	27	4.27	
K	39.2	6.18	
16 O	128	20.18	
<hr/> $C^{64}N^4H^{21}KO^{10} + 6Aq$		634.2	100.00

II.				Laurent.	
64 C	.....	384	.... 62.11	.....	60.00
4 N	.....	56	.... 9.06		
27 H	.....	27	.... 4.37	.....	4.27
K	.....	39.2	.... 6.34	.....	5.62
14 O	.....	112	.... 18.12		
<hr/>					
$C^{64}N^4H^{21}KO^8 + 6Aq$		618.2	.... 100.00		

Hydrindin is slightly soluble in boiling alcohol.

### Flavindin.



LAURENT. *Compt. chim.* 1849, 200; *J. pr. Chem.* 47, 163.

*Formation.* By heating indin or bisulphisatyde with alcoholic potash.

*Preparation.* The mother-liquor from hydrindin, prepared according to 1 or 2, is mixed with an acid, and the precipitate thus formed, which is a mixture of sulphur, hydrindin (sometimes also indin), and flavindin, is thrown on a filter, and treated with weak ammoniacal water, which dissolves the flavindin. The filtrate is precipitated with hydrochloric acid, and the precipitate of flavindin washed and dried. — It is formed more abundantly when the solution in alcoholic potash has been boiled for a long time.

*Properties.* Flavindin is of a pale yellow colour; it crystallises from alcohol in needles, united in the form of stars.

				Laurent.	
48 C	.....	288	.... 73.28	.....	72.50
3 N	.....	42	.... 10.68		
15 H	.....	15	.... 3.82	.....	3.92
6 O	.....	48	.... 12.22		
<hr/>					
$C^{48}N^3H^{15}O^6$		393	.... 100.00		

Isomeric with indigo-blue and indin.

Flavindin when heated is almost entirely converted into a body which crystallises in needles resembling benzoic acid.

It is slightly soluble in boiling water.

### Flavindic Acid.

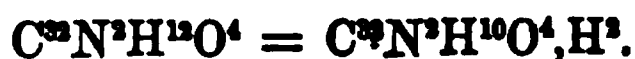


LAURENT. *Compt. chim.* 1849, 200.

The solution of flavindin in ammonia forms, with nitrate of silver, a yellow precipitate, which yields 42.2 per cent of silver on ignition, corresponding to the formula  $C^{48}N^3H^{16}Ag^3O^{12}$ . (The calculated percentage is 41.8.)

\* = 3 Atoms of Indigo-blue.

## Indigo-white.



PROUST. 1805. *Gilb.* 25, 451.

CHEVREUL. *Ann. Chim.* 66, 8; 68, 284; *Gilb.* 41, 345; 42, 315; *Dict. fc. nat.* 23, 391.

BERZELIUS. *Auf.* 7, 204; *Pogg.* 10, 126.

LIEBIG. *Mag. Pharm.* 18, 192; *Schw.* 51, 60.

DUMAS. *Ann. Chim. Phys.* 63, 265; *J. pr. Chem.* 10, 222.

*Colourless Indigo, deoxidised Indigo, reduced Indigo, Indigogen, Indigotine.*

The formation of indigo-white by the action of nascent hydrogen, appears to have been first remarked by Proust. Chevreul was the first to isolate it. Concerning the opinion that indigo-white is contained in the sap of the indigo-plant, see page 36.

*Formation.* By the action of deoxydising agents upon indigo-blue in the presence of alkalis (p. 44).

*Preparation.* Commercial indigo, purified by boiling with hydrochloric acid, next with strong potash, and afterwards with alcohol, is mixed with freshly prepared hydrate of lime (2 parts of quick lime to 1 of indigo) and placed in a closed vessel with 150 parts of boiling water, after which sulphate of iron equal to one-third the weight of the indigo is added, and after the vessel has been closed the whole is carefully shaken. (Dumas employed a small cask holding about 100 litres, in which he reduced half a kilogramme of indigo-blue.) After two days, the solution is decanted by means of a syphon into flasks filled with carbonic acid, and when the flasks are nearly full, they are completely filled with boiling dilute hydrochloric acid, corked up, and placed in a vessel containing cold water. The air is thus prevented from obtaining access to the indigo-white, which separates out in white crystalline flakes. After the indigo-white has settled down, the solution is drawn off with a wide syphon, and the deposit is thrown upon a filter, which is covered with a bell-jar, into which a stream of hydrogen or carbonic acid is passed. The filter is washed with water, which has been well boiled and then corked up. Indigo-white is very easy to wash, and if the deposit is allowed to stand for several days, it becomes so consistent that it may be washed in the air without becoming deeply coloured; warm water greatly accelerates the conversion of the indigo-white into indigo-blue. After the contents of the filter have been washed, they are spread, while still moist, upon a glass-plate and dried in vacuo. When the indigo-white is dry, carbonic acid is allowed to flow into the receiver of the air-pump, in order that the pores of the dry mass may become filled with the gas. (Berzelius, Dumas.) — 3 parts of indigo, which have been purified by boiling, are digested for 24 hours with 5 parts of hydrate of lime, 4 parts of sulphate of iron, and 120 parts of water, in a closed flask filled with hydrogen, and the whole is frequently shaken till the deposit assumes a greenish yellow and the solution a reddish yellow colour. The lime is precipitated from the latter with carbonate of potash, and the clear solution is decanted by means of a syphon filled with hydrogen, into a flask containing a mixture of hydrochloric acid and sulphite of ammonia. The thick white precipitate which



is thus formed is filtered out of contact with the air, washed with water containing a little sulphite of ammonia, and dried at  $100^{\circ}$  in a stream of hydrogen. In this process, the surface of the white indigo becomes oxidised, and the lower part becomes dirty white. (Liebig.) — Chevreul extracted commercial *woad* first with water and then repeatedly with boiling alcohol; when the alcohol was distilled from the alcoholic extract, purple laminæ were first deposited, and then when the solution was allowed to cool slowly, white grains and flakes, which turned blue in the air. He considered this product to be indigo-white.

*Properties.* Greenish white (probably quite white when perfectly pure), with a slightly silky lustre. (Berzelius.) Inodorous, tasteless, and without action upon litmus. (Berzelius, Liebig.)

					Dumas.
32 C .....	192	...	72.71	.....	72.02
2 N .....	28	...	10.63		
12 H .....	12	...	4.54	.....	4.75
4 O .....	32	...	12.12		
<hr/>					
$C^{32}N^2H^{12}O^4$ .....	264	...	100.00		

*Decompositions.* 1. When indigo-white is heated in vacuo, a little water is evolved, a small quantity of indigo-blue sublimes, and there remains a large carbonaceous residue. (Berzelius.) — 2. When exposed to the air and to the contact of various oxygen-compounds, it takes up oxygen and is converted into indigo-blue. — Freshly precipitated indigo-white turns blue immediately when shaken with water containing air, even if a free acid is present. (Giobert maintained that the presence of acids, and even of carbonic acid, prevents the oxidation.) After washing, and while still moist, it becomes purple through its entire mass on exposure to the air, unless it is rapidly dried. When dry, it must be exposed to the air for several days to become entirely oxidised, first becoming bright blue, and then dark blue through the entire mass. It cannot be preserved in sealed tubes, since the air contained in its pores is sufficient for its conversion into indigo-blue. Dry indigo-white exposed to the air at a gradually increasing temperature suddenly becomes dark purple. — When a cupric salt is added to an alkaline solution of indigo-white, a salt of the alkali together with indigo-blue and cuprous oxide are formed; the latter, on the addition of sulphuric acid, is decomposed into cupric oxide, which dissolves, and a residue of metal. — 3. Indigo-white precipitated from an alkaline solution by nitric acid, is turned blue by a slight excess of the acid, and then more completely decomposed. (Berzelius.) — Indigo-white dissolves instantly in sulphuric acid, and imparts to it a dark purple colour, which passes to blue on dilution. According to Berzelius, the indigo-white is oxidised, and part of the sulphuric acid converted into hyposulphuric acid.

*Combinations.* Indigo-white is insoluble in water, and in such acids as do not decompose it.

*With Metallic Bases.* Indigo-white combines with most metallic bases, forming compounds which oxidise rapidly in the air; those which



are insoluble are oxidised the most rapidly on account of their more finely divided state.

Indigo-white dissolves readily in all aqueous *alkalis* and also in the aqueous carbonates of ammonia, potash, and soda, and, according to Liebig, without depriving them of their alkaline reaction. The cold solutions are pure yellow, the warm and highly concentrated solutions burnt yellow. The air immediately separates indigo-blue from them; and as the surface becomes blue, a darker coloration, which passes to burnt yellow and red, may be observed directly beneath it. If the solution contains at the same time a reducing agent, the indigo-blue formed by the action of the air is continually reduced by its agency and redissolved. (Berzelius.)

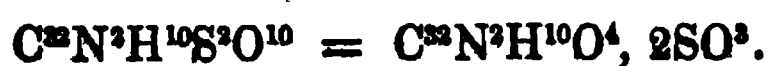
Indigo-white forms with *lime* a neutral compound readily soluble in water, and a basic compound which is almost insoluble; this latter is precipitated when the solution of the more neutral body is digested with hydrate of lime, or when indigo is digested with water, sulphate of iron, and an excess of lime. The precipitate of gypsum and hydrated sesquioxide of iron which is formed at the same time, may be readily suspended in water and separated by levigation. The basic compound is of a lemon-yellow colour, and very slightly soluble in water, to which it imparts a yellow colour. On exposure to the air, it first turns green and then bright blue. (Berzelius.)

The compounds of indigo-white with the *earths and heavy metallic oxides* are obtained when a suitable crystalline salt of one of these bases is added to an aqueous alkaline solution of indigo-white. — The compound of indigo-white and *magnesia*, obtained from sulphate of magnesia is, on account of its slight solubility, partly thrown down as a white precipitate, and partly remains dissolved in the aqueous solution, to which it imparts a yellow colour; it turns blue on exposure to the air. — The compound of indigo-white and *alumina* is white, but rapidly turns blue on the filter; if it be then dried, it forms a dark blue crystalline powder which sparkles in sunshine; indigo-blue may be very readily sublimed from it and a grey earthy residue then remains. (Berzelius.)

The compound of indigo-white with *protoxide of manganese* is dirty green; when dried in the air and heated, it does not yield any sublimate of indigo-blue. (Berzelius.) — The compound with *oxide of zinc* is white, but rapidly turns blue on exposure to the air, and then yields a sublimate of indigo-blue on heating. (Berzelius.) — The compound with *oxide of lead* is white and slightly crystalline; it turns rapidly blue on exposure to the air, and if it be then heated, detonates slightly, and yields reduced lead. — The compound with *protoxide of iron* is white, but quickly turns blue on exposure to the air; if it be then heated, it does not yield any sublimate of indigo-blue. — The compound with *protoxide of cobalt* is grass-green, and when dried in the air, does not yield any sublimate of indigo-blue on heating. — Nitrate of *silver* produces with an aqueous solution of the potash compound a precipitate which is at first transparent brown and then becomes black; it is not acted upon by the air, and when heated produces a gentle explosion and yields a sublimate of indigo-blue and a residue of metallic silver. (Berzelius.)

Indigo-white is soluble in *alcohol*. (Liebig, Berzelius.) The solution turns blue on exposure to the air and deposits indigo-blue. (Berzelius.) — It is soluble in *ether*, to which it imparts a yellow colour; the solution turns green on exposure to the air and then inclines to purple, but does not begin to deposit indigo-blue until a large quantity of ether has evaporated. (Berzelius.)

## Sulphophœnicic Acid.



CRUM. *Ann. Phil.* Febr. 1823; *Schw.* 38, 50.

BERZELIUS. *Lehrb. Aufl.* 3, 70; *Pogg.* 10, 189.

DUMAS. *N. Ann. Chim. Phys.* 2, 204; *J. pr. Chem.* 24, 200; *Pharm. Centr.* 1841, 598.

HÄFFELY.

*Indigo-purple, Phœnicin, Sulphopurpuric Acid, Phœnicinschwefelsäure.*

Formed when sulphuric acid is allowed to act upon indigo for a short time, or not in excess (p. 43).

*Preparation.* 1 part of indigo-blue is mixed with from 8 to 10 parts of strong sulphuric acid, and kept for three days at a temperature of 50° or 60°; the solution is then diluted with water and the precipitate of sulphophœnicic acid filtered, washed with dilute hydrochloric acid, and dried in an oil-bath at 80°—100°; the temperature should not exceed 200°. (Dumas.) —2. Powdered indigo is purified by boiling with dilute sulphuric acid, and then shaken up with from 7 to 8 parts of strong sulphuric acid till the mixture becomes olive-green. The whole is then diluted with a very large quantity of water, and the precipitate of sulphophœnicic acid is collected on a filter and washed with water, which becomes more deeply blue in proportion as the sulphuric acid is removed. The last filtrates are evaporated to dryness. (Crum.) Berzelius uses pure indigo-blue. —3. As the extraction of the sulphophœnicic acid on the filter according to (1) is a very slow process, and when the greater part of the indigo-blue is converted into sulphophœnicic acid by the prolonged action of the sulphuric acid, water will no longer pass through the filter, the following method may be employed, which yields a more abundant, though less pure product. —1 part of powdered indigo is shaken in a flask with 10 parts of strong sulphuric acid, till the blue colour which the indigo had at first lost is completely restored. For this purpose, from 10 to 12 hours are requisite at 7°, 3 hours in the heat of the sun, 20 minutes at 38°, and a few moments at 100°. A large quantity of water is added; the solution is filtered; and the precipitate is taken from the filter and washed by decantation with water containing sufficient chloride of ammonium to prevent it from dissolving the sulphophœnicic acid. The solution of chloride of ammonium is allowed to run from the filter, and the precipitate is removed and suspended in a large quantity of water. After three days, the solution is poured off and the water is renewed as long as sulphophœnicic acid continues to dissolve. The sulphophœnicic acid is then precipitated from the decanted solutions by chloride of potassium, and the precipitate is washed on a filter with water as long as the water continues to pass through. — Sulphophœnicic acid thus obtained contains a little potash-salt and a large quantity of earthy matter; after drying, it is no longer soluble in water. (Crum.)

Häffely triturates 1 part of finely powdered indigo with 20 parts of common sulphuric acid; allows the whole to stand for some time, till a drop of the solution, which is at first blue, colours water or paper

violet; and then mixes the solution with a large quantity of water: the action of the sulphuric acid is promoted by heating the whole to  $40^\circ$ . If less sulphuric acid is used, it must be heated more; if only 3 parts of sulphuric acid are employed for 1 part of indigo, the latter is not completely converted into sulphophœnicic acid. If fuming sulphuric acid is used, it is not easy to discover when the reaction is ended.

*Properties.* Sulphophœnicic acid forms a blue mass (Crum); a purple-red powder. (Berzelius, Dumas.)

				Dumas.
32 C .....	192	...	56.14	55.11
2 N .....	28	...	8.19	
10 H .....	10	...	2.92	3.00
2 $SO^2$ .....	80	...	23.39	24.20
4 O .....	32	...	9.36	
<hr/>				
$C^{32}N^2H^{10}O^4, 2SO^2$ .....	342	...	100.00	

*Decompositions.* 1. It dissolves readily, with blue colour in sulphuric acid, especially in the fuming acid, being at the same time gradually converted into sulphindigotic acid.

2. With a large quantity of soda-ley, it forms a yellow solution which turns blue if immediately mixed with sulphuric acid of  $66^\circ$  B. but if oil of vitriol is added after 24 hours, it produces a whitish precipitate. (Gros-Renaud, *Dingl. pol. J.* 129, 288.)

*Addition to Sulphindigotic Acid.* When sulphindigotate of potash is stirred up with water, and caustic soda of  $38^\circ$  B. is added, a deep yellow solution is formed, containing in suspension a black precipitate, which, if thrown on a filter and washed, colours the water blue, and the more deeply the weaker the alkaline reaction. If the yellow solution together with the precipitate, is immediately mixed with sulphuric acid, a blue liquid is formed, which becomes green after 24 hours, and then violet, and dyes wool blue. After the lapse of 48 hours, an intensely red solution is formed with sulphuric acid; and if carbonate of soda is added to this solution till but little acid reaction is left, it dyes wool dark rose-red or amaranth-red. This colouring matter is removed from the wool by sulphuric acid; it forms with caustic soda, a yellow solution, which after 24 hours, becomes amaranth-red on the addition of sulphuric acid. If caustic soda is allowed to act for three days upon indigo-red, a red solution and a brown precipitate are formed. (Gros-Renaud.)

3. The solutions of the sulphophœnicates are reduced to yellow liquids by heating with sulphuretted hydrogen, by sulphate of iron and lime, or by caustic alkalis. The reduced solutions turn blue on exposure to the air, and on the addition of other salts, the salt of sulphophœnicic acid is precipitated unchanged. (Berzelius.)

*Combinations.* Sulphophœnicic acid is soluble in water, to which it imparts a blue colour.

The *Sulphophœnicates* are precipitated from the aqueous solution of the acid by the addition of other salts. When dry they are red; their aqueous solutions are blue. They dissolve very sparingly in water, but more readily in alcohol. (Crum, Berzelius.)

When *Sulphophœnicate of Ammonia* is heated, it evolves sulphurous acid together with sulphite of ammonia and a red vapour, which yields a sublimate like indigo-blue. This sublimate is often bright green on the lowest edges, like the wing-cases of cantharides, and turns brown when burnished. (Berzelius.)

*Sulphophœnicate of Potash.* — The aqueous solution of the acid is precipitated by a solution of acetate of potash and the flocculent purple precipitate is washed, first with aqueous acetate of potash and then with alcohol. It dissolves in 100 parts of water. When ignited it leaves 21·4 per cent.  $\text{KO}, \text{SO}^3$ . (Dumas.) (The formula  $\text{C}^{22}\text{N}^3\text{H}^9\text{KO}^4, 2\text{SO}^3 + 2\text{Aq}$  requires 21·9 per cent.  $\text{KO}, \text{SO}^3$ .)

Common salt precipitates sulphophœnicic acid prepared by the second method, from its solution in 60 times its weight of water; sulphate of magnesia, sulphate of zinc and sulphate of copper precipitate the acid from 2000 times its weight of water; protosulphate of iron, from 3000 times its weight; and chloride of calcium and alum, from 8000 times its weight. (Crum.)

When a solution of indigo in sulphuric acid is saturated with carbonate of lime and the precipitate washed, there remains a red mixture of gypsum and sulphophœnicate of lime. If the gypsum is decomposed by digestion with carbonate of potash and the resulting carbonate of lime dissolved with hydrochloric acid, the sulphophœnicate of lime may be extracted from the dark red residue by a large quantity of boiling alcohol. (Berzelius.)

Sulphophœnicic acid forms a blue solution with alcohol. (Crum.)

### Isatan.



LAURENT: *Rev. scient.* 10, 298; *J. pr. Chem.* 28, 346.

Isatan is sometimes formed when bisulphisatyde is boiled with bisulphite of ammonia, as a white powder, which, when it is mixed with the needles which are commonly formed by a similar treatment of sulphisatyde, must be boiled with a rather large quantity of alcohol. The residue dissolved in a large quantity of alcohol yields crystals on cooling, which appear under the microscope, either as rectangular or pointed ovals according to the side which is viewed.

					Laurent.
32 C .....	192	...	68·57	.....	68·72
2 N .....	28	...	10·00	.....	10·50
12 H .....	12	...	4·28	.....	4·36
6 O .....	48	...	17·15	.....	16·42
<hr/>					
$\text{C}^{22}\text{N}^3\text{H}^{12}\text{O}^6$ .....	280	...	100·00	.....	100·00

Isatan heated till it melts, turns brownish red and yields a mixture of isatin and indin:



It is decomposed by boiling nitric acid, with formation of a violet powder similar to nitrindin. With alcoholic potash, it forms a yellow solution, from which water precipitates hydrindin, and hydrochloric acid a mixture of isatin with a resinous substance.

Isatan is very slightly soluble in alcohol.



## Isatyde.



ERDMANN. (1841.) *J. pr. Chem.* 24, 15; *Pharm. Centr.* 1841, 710.

LAURENT. *N. Ann. Chim. Phys.* 3, 382; *J. pr. Chem.* 25, 436; *Pharm. Centr.* 1842, 248; *Compt. chim.* 1849, 208; *Ann. Pharm.* 72, 282.

*Isathyde.*

*Formation.* By the action of deoxidising agents upon isatin, *e. g.* of nascent hydrogen, and of sulphuretted hydrogen :



*Preparation.* 1. Powdered isatin is heated in a flask with a piece of zinc foil, a large quantity of water and a little sulphuric acid. As the isatin dissolves, it takes up the nascent hydrogen, and is converted into a pulverulent isatyde, which is washed with water and then boiled with alcohol to remove any undecomposed isatin that may be present. (Laurent.)—2. *a.* Isatin dissolves completely in warm sulphide of ammonium, and the solution on cooling deposits a white, slightly yellow, or reddish powder, which is free from sulphur after it has been washed, and turns pale-red on drying. (Erdmann.)—*b.* To a solution of isatin in hot alcohol, a little bisulphide of ammonium is added and the mixture is allowed to stand in a stoppered bottle; in a few minutes small white scales begin to separate out and continue to do so for several days. After eight days, the greyish white precipitate is washed with alcohol on a filter, and the sulphur is extracted from the dry residue with bisulphide of carbon. (Laurent.)

*Properties.* Isatyde prepared according to 2 *b*, forms white or slightly grey crystalline laminæ, which appear under the microscope as oblique rectangular prisms (Laurent); prepared according to (1), it forms a pale-red slightly crystalline powder. (Erdmann.) It is tasteless and inodorous. (Laurent.)

							Erdmann.
32 C	.....	192	...	64·86	....	68·38	..... 68·14
2 N	.....	28	...	9·46			
12 H	.....	12	...	4·05	....	4·34	..... 4·42
8 O	.....	64	...	21·63			
<hr/>							
C <sup>32</sup> N <sup>2</sup> H <sup>12</sup> O <sup>8</sup>	.....	296	...	100·00			
Erdmann.					Laurent.		
					(2 b.)	(1.)	
32 C	.....	67·60	....	66·96	.....	65·28	.... 64·6
2 N	.....		....		.....	9·50	
12 H	.....	4·39	....	4·37	.....	4·10	.... 4·0
8 O	.....		....		.....	21·12	
<hr/>							
C <sup>32</sup> N <sup>2</sup> H <sup>12</sup> O <sup>8</sup>	.....		....		.....	100·00	

Erdmann examined various preparations of isatyde obtained according to 2 *a*.; he assigned to it the formula  $C^{16}NH^1O^4$  ( $= C^{32}N^2H^{12}O^8$ ), which requires 68.57 per cent. C., and 4.28 per cent. H. According to Laurent's formula, it bears the same relation to isatin as white to blue-indigo.

\* = 2 Atoms of Isatin + 2 H.

*Decompositions.* 1. Isatyde softens on heating and then turns violet-brown (forming a mixture of indin and isatin? Gerhardt); if more strongly heated till it is half melted, it decomposes and yields a substance which is soluble in alcohol, and is deposited from the alcoholic solution on evaporation in reddish brown crystals, which are soluble in potash, and are reprecipitated unchanged by acids. (Laurent.) When isatyde is heated in a test-tube, it decomposes and leaves a residue of difficultly combustible charcoal; it burns in the air with a luminous flame. — 2. It is decomposed by boiling *nitric acid*, a violet powder being first formed (in all probability nitrindin), which dissolves by continued boiling and the solution then deposits yellow flakes on the addition of water. — 3. It forms with alcoholic potash, isatic acid and indin, which, on continuing the action, is converted into hydrindin, flavindin and other products of decomposition :



(Compare Gerhardt, *Traité* 3, 609.) On treating isatyde with alcoholic potash, Laurent obtained a beautiful rose-coloured solution, from which isatin and hydrindin were precipitated on the addition of hydrochloric acid (p. 89); in a second experiment, the solution deposited black crystals of indin-potassium; in a third experiment, on heating the solution and adding water, a dirty rose-coloured oil separated out, and isatin was precipitated from the solution on the addition of hydrochloric acid. — Erdmann, by treating isatyde with potash, obtained a dark red solution which became colourless when heated, and yielded a crystalline salt on cooling; it gave yellow flakes with hydrochloric acid.

Isatyde is scarcely soluble in water.

It dissolves very slightly in boiling alcohol and ether.

### Bibromisatyde.



ERDMANN. (1841.) *J. pr. Chem.* 22, 260 and 262.

Prepared from bibromisatin in the same manner as bichlorisatyde from bichlorisatin (p. 102).

It is of a pale yellow colour, but becomes rose-coloured on drying at 100°, without losing weight.

	At 100°.		Erdmann.	
32 C .....	192	....	31.37	..... 32.42
2 N .....	28	....	4.57	
4 Br.....	320	....	52.29	
8 H .....	8	....	1.31	..... 1.91
8 O .....	64	....	10.46	
<hr/>				
$\text{C}^{12}\text{N}^2\text{Br}^4\text{H}^8\text{O}^8$ .....	612	....	100.00	

Heated above 100°, it gives off water and turns brown. It decomposes below 220° into bromisatin, bibromindin, and water.

## Chlorisatyde.



ERDMANN. (1839.) *Ann. Pharm.* 33, 129; *J. pr. Chem.* 22, 260; 24, 6; *Pharm. Centr.* 1840, 116; 1841, 210.

LAURENT. *N. Ann. Chim. Phys.* 3, 382; *J. pr. Chem.* 25, 436.

## Chlorisathydase.

**Formation.** By the action of sulphide of ammonium upon chlorisatin.

**Preparation.** Chlorisatin is dissolved in sulphide of ammonium, and allowed to stand in a stoppered flask; after some time (more rapidly on warming) the liquid becomes turbid, and deposits a reddish or yellowish white precipitate, which must be rapidly washed with water from which the air has been removed by boiling. (If the sulphide of ammonium is not freshly prepared and contains free ammonia, the colour of the precipitate approaches to violet.)

**Properties.** Chlorisatyde is a whitish powder which turns reddish at  $120^\circ$ , without changing its weight. From its boiling alcoholic solution it is deposited in crystalline crusts on cooling.

					Erdmann.		Laurent.
32 C	.....	192	...	52.63	.....	52.23	.... 52.05
2 N	.....	28	...	7.67	.....		.... 7.56
2 Cl	.....	70.8	...	19.40			
10 H	.....	10	...	2.74	.....	2.89	.... 2.80
8 O	.....	64	...	17.56			
<hr/>							
$C^{32}N^2Cl^3H^{10}O^3$	....	364.8	....	100.00			

**Decompositions.** 1. Chlorisatyde begins to give off water at  $180^\circ$ ; at  $200^\circ$  more is evolved, but the evolution of water does not cease till the temperature has exceeded  $200^\circ$ . When it is carefully heated in vacuo up to  $220^\circ$ , crystals of chlorisatin sublime, and there remains a residue containing a mixture of chlorisatin and chlorindin with a little undecomposed chlorisatyde:



— 2. When suspended in water, it is but slightly attacked by chlorine, merely assuming a slightly reddish or pale violet colour.— 3. Heated with *potash* it forms chlorisatic acid, chlorindin, and chlorisatydic acid, without absorption of oxygen or evolution of any gas.— 4. Chlorisatyde is turned red by *caustic ammonia*, and dissolves partially when heated, forming a red solution which deposits a red powder on cooling.— 5. It dissolves abundantly in warm sulphide of potassium, and the solution, on cooling, deposits a powder, which appears to be undecomposed chlorisatyde.

Chlorisatyde is insoluble in cold water, and very slightly soluble in hot water.

It is slightly soluble in boiling alcohol.



**Chlorisatydic Acid.**

ERDMANN. *J. pr. Chem.* 22, 257; *Pharm. Centr.* 1841, 212.

**b Chlorisatic acid.**

Chlorisatyde dissolves readily in warm potash, and forms a yellow solution which deposits chlorisatate of potash on cooling; the mother-liquor gives, with hydrochloric acid, a bright yellow precipitate, the greater part of which dissolves in boiling water, leaving a residue of chlorindin. The precipitate obtained by adding hydrochloric acid to the aqueous solution is of a still purer yellow, and is almost completely soluble in boiling water. The aqueous solution, on cooling, deposits the chlorisatydic acid as a lemon-coloured powder.

The salt obtained by dissolving chlorisatydic acid in potash can be obtained only in ill-defined crystals by slow evaporation; if the solution is more rapidly evaporated, the salt separates in semi-fluid flakes, or as a thick oil. If the product is pressed, the adhering potash saturated with carbonic acid, and the salt dissolved out with alcohol, its aqueous solution forms, with acetate of lead, sulphate of copper, and chloride of barium, yellow precipitates, which are not acted upon in the cold, but redissolve in the solution when heated, and are reprecipitated in the pulverulent form on cooling.

**Sulphochlorisatin.**

ERDMANN. (1841.) *J. pr. Chem.* 22, 260; 24, 6; *Pharm. Centr.* 1841, 209.

**Formation.** By the action of sulphuretted hydrogen upon chlorisatin.

**Preparation.** When sulphuretted hydrogen is passed through an alcoholic solution of chlorisatin, a white precipitate is formed which increases on diluting the solution saturated with sulphuretted hydrogen. It is freed from any sulphur it may contain by bisulphide of carbon.

I.			
32 C .....	192	....	41.67
2 N .....	28	....	6.08
2 Cl .....	70.8	....	15.36
10 H .....	10	....	2.17
10 S .....	160	....	34.72
<hr/>			
$\text{C}^{32}\text{N}^2\text{Cl}^3\text{H}^{10}\text{S}^{10}$ .....	460.8	....	100.00

\* = Chlorisatyde + 2HO?.



II.				Erdmann.	
32 C	.....	192	....	44.66	.... 41.70
2 N	.....	28	....	6.67	
2 Cl	.....	70.8	....	16.51	
10 H	.....	10	....	2.33	.... 2.37
8 S	.....	128	....	29.83	.... 31.09
<hr/>					
$C^{32}N^2Cl^2H^{10}S^8$	.....	428.8	....	100.00	

Calculation I. is according to Erdmann; II. is according to Gerhardt. — Compare Laurent, *N. Ann. Chim. Phys.* 3, 382.

### Bichlorisatyde.



ERDMANN. (1839.) *Ann. Pharm.* 33, 129; *J. pr. Chem.* 22, 260; 24, 9; *Pharm. Centr.* 1840, 116; 1841, 210.

LAURENT. *N. Ann. Chim. Phys.* 3, 481.

#### Chlorisathydèse.

*Formation.* By the action of sulphide of ammonium upon bichlorisatin (p. 78).

*Preparation.* It is prepared from bichlorisatin like chlorisatyde from chlorisatin (p. 100).

*Properties.* Resembles chlorisatyde. Assumes a pale rose-colour at  $120^\circ$ .

				Erdmann.	
32 C	.....	192	....	44.28	..... 44.70
2 N	.....	28	....	6.46	
4 Cl	.....	141.6	....	32.66	
8 H	.....	8	....	1.84	..... 2.16
8 O	.....	64	....	14.76	
<hr/>					
$C^{32}N^2Cl^4H^8O^8$	.....	433.6	....	100.00	

*Decompositions.* 1. Bichlorisatyde decomposes below  $220^\circ$  into bichlorisatin, bichlorindin, and water. — 2. It dissolves in warm potash without evolving ammonia, even when air is excluded, and forms a yellow solution, from which bichlorisatydate of potash crystallises on cooling. Hydrochloric acid added to the mother-liquor precipitates a mixture of bichlorisatydic acid and bichlorindin, and the filtrate from these products turns dark orange-red when heated, and deposits bichlorisatin on cooling. — 3. It is reddened in the cold by cold caustic ammonia; on heating, it partly dissolves, and forms a red liquid which deposits a red powder on cooling.

Bichlorisatyde is insoluble in cold water, and very slightly soluble in boiling water.

It does not dissolve in cold but only in boiling alcohol.

**Bichlorisatydic Acid.**

ERDMANN. *J. pr. Chem.* 22, 267; *Pharm. Centr.* 1841, 213.

b *Bichlorisatic acid.*

*Formation.* By the action of potash upon bichlorisatyde.

*Preparation.* The yellow solution obtained by warming bichlorisatyde with potash is mixed with acetic acid, the resulting precipitate dissolved in potash, and the solution precipitated by hydrochloric acid. (If the solution of bichlorisatyde in potash is precipitated with hydrochloric acid instead of acetic acid, the precipitate is contaminated with bichlorisatin, and forms a dark orange-red solution with potash.)

*Properties.* Light yellow powder, soluble in boiling water.

					Erdmann.	
					a.	b.
32 C	.....	192	...	44.08	.....	44.38
2 N	.....	28	...	6.43	.....	45.4
4 Cl	.....	141.6	...	32.50	.....	
10 H	.....	10	...	2.30	.....	2.40
8 O	.....	64	...	14.69	.....	2.3
<hr/>						
$C^{32}N^2Cl^4H^{10}O^8$	.....	435.6	...	100.00		

The *potash-salt* forms yellow crystalline scales, very similar to bichlorisatate of potash. It is readily soluble in water and in alcohol.

The aqueous solution forms, after a while, with acetate of copper, yellow flakes which dissolve in boiling water and crystallise out on cooling; with acetate of lead it forms yellow flakes, which dissolve in boiling water and are precipitated, on cooling, as a powder; with nitrate of silver it forms yellow flakes which become brownish on boiling.

**Sulphisatyde.**

LAURENT. (1841.) *N. Ann. Chim. Phys.* 3, 463; *J. pr. Chem.* 25, 438; *Pharm. Centr.* 1842, 250.

*Sulphasatyde.*

*Formation.* By the action of potash on bisulphisatyde.

*Preparation.* When potash is added, drop by drop, to an alcoholic solution of bisulphisatyde, the liquid immediately turns red, and in a few seconds yields a white crystalline precipitate. After the precipitate has stood for 24 hours, it is washed on a filter with boiling alcohol and then dried. It generally has a faint rose-colour, owing to the presence of a little indin. It is difficult to avoid the formation of this latter substance, which is often present in such quantity, that the product cannot be used for the preparation of sulphisatyde.

*Properties.* Sulphisatyde forms a white, crystalline, inodorous and tasteless powder; it crystallises from hot alcohol in microscopic rectangular scales.

	At 100°.			Laurent.	
32 C .....	192	...	61.54	.....	61.70
2 N .....	28	...	8.97	.....	9.24
12 H .....	12	...	3.85	.....	3.90
2 S .....	32	...	10.25	.....	11.04
6 O .....	48	...	15.39	.....	14.12
<hr/>					
C <sup>32</sup> N <sup>2</sup> H <sup>12</sup> S <sup>2</sup> O <sup>6</sup> ....	312	...	100.00	.....	100.00

*Decompositions.* 1. Sulphisatyde, when heated, melts, turns red, swells up, and decomposes, while sulphuretted hydrogen is evolved, and a rose-coloured oil distils over, together with the vapours of a substance which crystallises in needles; finally, there remains a bulky residue of charcoal.—2. It is converted by nitric acid into a violet powder, which, in all probability, is nitrindin; the solution contains sulphuric acid.—3. It is decomposed by cold potash, with formation of various products, among which is indin; the solution evolves sulphuretted hydrogen on the addition of hydrochloric acid, and gives a precipitate consisting of sulphur and a little reddish matter. On treating sulphisatyde with warm potash, hydrindin is formed.

Sulphisatyde is insoluble in water. Boiling alcohol dissolves only traces, which separate in small crystalline scales on cooling. It is not more soluble in ether than in alcohol.

### Bisulphisatyde.



ERDMANN. (1841.) *J. pr. Chem.* 24, 16; *Pharm. Centr.* 1841, 711.

LAURENT. *N. Ann. Chim. Phys.* 3, 463; *J. pr. Chem.* 25, 438; *Pharm. Centr.* 1842, 249; *Compt. rend.* 14, 492; *Rev. scient.* 10, 298; *J. pr. Chem.* 28, 346.

*Sulphisatin. Sulphèsathyde.*

*Formation.* By the action of sulphuretted hydrogen upon isatin.

*Preparation.* When sulphuretted hydrogen is passed through a boiling concentrated alcoholic solution of isatin, the liquid becomes pale yellow, and forms a crystalline deposit, which increases on cooling, and consists of microscopic sulphur-crystals and scales (probably of isatyde). The solution is allowed to stand for a week, that the greater part of the sulphur may crystallise out; it is then poured off and mixed with a little water, and the resulting precipitate is removed, as it contains sulphur; it is then shaken up with more water, which precipitates the bisulphisatyde as a brownish grey resinous substance. (Laurent.) Erdmann precipitated the solution which had been separated from the precipitate produced by sulphuretted hydrogen, immediately with water; the precipitated yellowish white flakes united into lumps on heating.

*Properties.* Bisulphisatyde, when dried, is a yellowish grey, inodorous, and tasteless powder. It does not crystallise from its alcoholic or ethereal solution, either on cooling or by spontaneous evaporation. (Laurent.) Dried at 110° it always becomes bluish or brick-red; if the solution is exposed to the air for some time before the addition of water, the precipitate is brownish red. (Erdmann.)

					Erdmann.	Laurent.
32 C	.....	192	...	58.54	..... 53.51	.... 57.64
2 N	.....	28	...	8.53		
12 H	.....	12	...	3.66	..... 3.40	.... 3.81
4 S	.....	64	...	19.51	..... 24.49	.... 20.10
4 O	.....	32	...	9.76		
<hr/>						
C <sup>32</sup> N <sup>2</sup> H <sup>12</sup> S <sup>4</sup> O <sup>4</sup>	.....	328	...	100.00		

Erdmann attributes but little value to his analysis. Laurent obtained too small a quantity of carbon, because his substance contained a little free sulphur.

*Decompositions* 1. Swells up strongly when heated in a glass tube and melts with evolution of sulphuretted hydrogen; at the same time a brown oil and a needle-shaped sublimate are formed, and there remains a bulky residue of charcoal. — 2. Boiled with strong *nitric acid*, it puffs up, evolves hyponitric acid, and dissolves; water precipitates yellow flakes from the solution. In boiling nitric acid diluted with its own bulk of water, it puffs up and gives off nitrous fumes. If the reddish-brown swollen mass is treated after a few minutes with alcohol, the latter takes up a reddish substance, which is insoluble in water but soluble in potash, from which it is precipitated by acids. The portion insoluble in alcohol dissolves in potash, and on neutralising the solution with an acid, a white precipitate is formed, insoluble in water, and consisting of microscopic needles. The liquid obtained by the action of nitric acid contains sulphuric acid, but no oxalic acid. — 3. *Bromine* acts violently upon bisulphisatyde, with evolution of bromide of sulphur and hydrobromic acid, and forms a yellow mass containing bromindin, an orange-yellow crystalline mass, and a little resin. — 4. Bisulphisatyde dissolves in strong *sulphuric acid* with the aid of a gentle heat; the red solution is not precipitated by water; potash colours it green, but does not precipitate it. — 5. On treating bisulphisatyde with *potash*, sulphisatyde and various other products (amongst others, indin) are formed, which, however, cannot be produced at will. (According to Erdmann, the solution deposits a crystalline salt.) Ammonia behaves in a similar manner. — With bisulphite of ammonia various products are formed, amongst others, isatan and sulphisatanite of ammonia.

Bisulphisatyde is insoluble in boiling water, and very readily soluble in warm alcohol and ether.

### Sulphisatanous Acid.



LAURENT. (1843.) *Rev. scient.* 10, 298; *J. pr. Chem.* 28, 346.

*Formation.* By treating bisulphisatyde with bisulphite of ammonia.

**Preparation.** A solution of bisulphisatyde in a little alcohol is boiled with bisulphite of ammonia, whereupon the solution, which was at first clear, deposits an abundant greyish precipitate, which is filtered off. The filtrate is evaporated to dryness, the residue dissolved in water, and the solution is filtered and carefully evaporated; it then yields white crystals of sulphisatanite of ammonia. The crystals are dissolved in alcohol, the solution mixed with alcoholic bichloride of platinum; the chloroplatinate of ammonium filtered off; and the excess of platinum precipitated from the solution by sulphuretted hydrogen: the filtrate yields crystals of the acid on evaporation.

**Properties.** Small leafy needles.

					Laurent.
16 C	.....	96	...	45.07	..... 48.5
N	.....	14	...	6.57	
7 H	.....	7	...	3.29	..... 3.6
2 S	.....	32	...	15.02	
8 O	.....	64	...	30.05	
$C^{16}NH^7S^2O^3$ .....					213 ... 100.00

Laurent had too small a quantity to purify the substance in a proper manner.

**Sulphisatanite of Ammonia.** — For preparation see above. When the solution will not crystallise properly, it is again evaporated to dryness, and the residue is extracted with boiling alcohol, from which the salt crystallises in small prisms; these are recrystallised from water by spontaneous evaporation. It forms large, pale yellow, right rectangular tables, one side of which is replaced by two faces inclined to each other at an angle of  $93^\circ$ . It loses 7.43 per cent. (or 2 atoms) of water when dried in vacuo at  $100^\circ$ .

<i>Crystallised.</i>				<i>Laurent.</i>	
16 C	.....	96	....	38.72	.... 39.9
2 N	.....	28	....	11.29	..... 10.8
10 H	.....	10	....	4.03	..... 4.1
2 S	.....	32	....	12.90	..... 14.2
8 O	.....	64	....	25.80	.....
2 HO	.....	18	....	7.26	..... 7.4
<hr/>					
$C^{16}NH^6(NH^4)S^2O^3 + 2Aq$	....	248	....	100.00	

Treated with hydrochloric acid, it neither evolves sulphuretted hydrogen nor produces any precipitate. No sulphuric acid is formed on passing chlorine through the aqueous solution. On evaporating the liquid, needles are obtained. — Sulphisatanite of ammonia is readily soluble in water, somewhat less soluble in alcohol.

### Imasatin.



LAURENT. (1842.) *N. Ann. Chim. Phys.* 3, 486; *J. pr. Chem.* 25, 458; *Pharm. Centr.* 1842, 260; *Rev. scient.* 14, 364; 18, 464; *J. pr. Chem.* 35, 114.

**Formation.** By the action of aqueous ammonia upon an alcoholic solution of isatin :



*Preparation.* When common alcohol is saturated with isatin, a little more isatin added, and the whole mixed with aqueous ammonia, a beautiful red solution is formed, which appears to contain isatate of ammonia; if it is immediately heated to boiling, a brown, soft, resinous precipitate is formed; but if left to itself for several days, it yields a grey crystalline precipitate or round brown grains. To purify the precipitate, it is boiled with potash and water, and chloride of ammonium is added; a yellowish precipitate is then immediately formed, which shrinks somewhat together; the liquid is then decanted, the precipitate dissolved in hot alcohol, and the solution allowed to cool. If the precipitate is heated to the boiling point together with the solution from which it was deposited, it becomes granular and insoluble in alcohol. (Formerly, Laurent dissolved the precipitate in as little warm potash as possible, then diluted the solution with alcohol, and neutralised it, while still warm, with hydrochloric acid; on cooling, the imasatin separated in ill-defined crystalline grains.)

*Properties.* Short yellowish prisms.

				Laurent.
82 C .....	192	...	65.53	64.99
3 N .....	42	...	14.33	14.40
11 H .....	11	...	3.75	3.93
6 O .....	48	...	16.39	16.68
<hr/>				
$C^{82}N^3H^{11}O^6$ .....	293	...	100.00	100.00

The substance analysed was purified by the older method.

*Decompositions.* 1. When heated, it melts, gives off ammonia and yields a sublimate of very oblique rhombs, which are after elongated in the form of needles, and leaves a large residue of charcoal. — 2. It is dissolved and decomposed by boiling nitric acid; the solution diluted with water deposits a large quantity of yellow flakes. — 3. It dissolves in sulphuric acid, and the solution mixed with water gives a white gelatinous precipitate; if however it is allowed to attract moisture gradually from the air, it deposits apparently unchanged imasatin in radiating granules. — 4. With bromine it gives off vapours of hydrobromic acid, and forms a yellow substance which is rather easily soluble in alcohol. — 5. It is not decomposed by boiling hydrochloric acid. — It does not form isatin when acted upon by alkalis or acids.

*Combinations.* Imasatin is insoluble in water. — It forms with potash a brownish solution from which it is precipitated by acids or by chloride of ammonium; the freshly precipitated imasatin is soluble in ammonia, but after it has been dried and crystallised, it no longer dissolves. The ammoniacal solution forms with nitrate of silver, a precipitate containing from 25.5 to 28 per cent. of silver; [the formula  $C^{82}N^3H^{10}AgO^6$  requires 27 per cent. L.]; and when decomposed by hydrochloric acid and mixed with alcohol and bichloride of platinum, it gives a precipitate containing 12 per cent. of platinum. The potash solution of imasatin forms with nitrate of silver a precipitate containing from 39 to 40 per cent. of silver.

Imasatin is very slightly soluble in boiling alcohol, and insoluble in ether.

**Bibromimasatin.**

LAURENT. (1841.) *N. Ann. Chim. Phys.* 3, 497.

*Imabromisatinèse, Imabibromisatin.*

*Formation and Preparation.* Bibromisatin is heated to boiling with an excess of absolute alcohol, and a stream of ammoniacal gas is passed through the solution, which then on cooling deposits, first bibromisatin as a powder consisting of microscopic reddish yellow needles, afterwards a redder powder: the first deposit must therefore be rapidly filtered off.

					Laurent.
32 C	.....	192	...	31.52	..... 31.3
3 N	.....	42	...	6.90	..... 7.4
4 Br	...	320	...	52.55	
7 H	.....	7	...	1.15	..... 1.4
6 O	.....	48	...	7.88	
<hr/>					
$C^{32}N^3Br^4H^7O^6$	.....	609	....	100.00	

It is decomposed by heat and yields a sublimate of needles. It dissolves in potash without evolution of ammonia; and a white gelatinous body is precipitated from the solution by acids. The potash solution of bibromimasatin, mixed with ammoniacal nitrate of silver, gives a precipitate which contains 24 per cent. of silver, and is probably bibromimasatinargent-ammonium =  $C^{32}N^3Br^4H^5(NAgH^2)^2O^6$ , the formula requiring 25 per cent. of silver.

**Chlorimasatin.**

LAURENT. (1841.) *N. Ann. Chim. Phys.* 3, 495.

*Formation and Preparation.* Chlorisatin dissolves readily in a boiling mixture of alcohol and ammonia. The solution after two days deposits yellowish brown grains; and when the mother-liquor is poured off from the deposit and mixed with water, a pale yellow precipitate is formed, which must be filtered off and extracted with boiling alcohol; chlorimasatin then remains in the form of a reddish powder. This latter appears to be identical with the first granular precipitate. The filtrate from the pulverulent chlorimasatin forms with hydrochloric acid a reddish brown resinous precipitate and the filtrate from the precipitate yields on evaporation a partly crystalline partly resinous residue; both are mixtures of chlorisatin, chlorimasatin and chlorisamic acid.

*Properties.* Chlorimasatin is very similar to imasatin.

				Laurent.	
32 C	.....	192	....	53.07	..... 52.5
3 N	.....	42	....	11.61	
2 Cl	.....	70.8	....	19.57	
9 H	.....	9	....	2.49	..... 2.7
6 O	.....	48	....	13.26	
<hr/>					
$C^{32}N^3Cl^2H^9O^6$	.....	361.8	....	100.00	

It dissolves in potash without evolution of ammonia, and the solution forms with acids a white gelatinous precipitate.

### Isamic Acid.



LAURENT. (1841.) *N. Ann. Chim. Phys.* 3, 490; *J. pr. Chem.* 25, 462; *Pharm. Centr.* 1841, 262.

*Imasatic acid, Isatinamic acid, Rubindenic acid.*

**Formation.** By the action of warm ammonia on isatin, the isatate of ammonia which is first formed being converted into isamate of ammonia:



**Preparation.** 1. Aqueous ammonia is allowed to act upon isatin at a moderate heat, whereby imasatin is precipitated, and the filtered solution is evaporated down and mixed with hydrochloric acid. A red precipitate is then formed consisting of isamic acid, which is mixed with amasatin, especially if only a small quantity of hydrochloric acid was employed, and must therefore be treated with as small a quantity as possible of dilute ammonia: the isamic acid then dissolves, and a mixture of amasatin and isatin generally remains behind. The ammoniacal solution is neutralised with hydrochloric acid, which immediately, or in a few minutes forms a brilliant red precipitate of the acid; this is washed on a filter with as little water as possible and recrystallised from boiling alcohol. — 2. It is better to saturate aqueous potash with isatin, evaporate the solution to dryness, dissolve in alcohol, and mix it with a warm and very concentrated solution of sulphate of ammonia (this must be added in a greater proportion than 1 atom to 1 atom of isatin). The precipitated sulphate of potash is filtered off, and the solution of isatate of ammonia is evaporated to a syrupy consistence, whereby it is converted into isamate of ammonia. It is then boiled with alcohol, the precipitate of sulphate of ammonia and amasatin is filtered off, and the filtrate is neutralised with hydrochloric acid and left to cool. If, in consequence of an excess of ammonia having been added, or of the crystals of isamic acid having been too long heated, the product is mixed with a little isatin, the latter may be separated by dissolving the crystals in very dilute ammonia.



*Properties.* Isamic acid forms beautiful, shining, rhombic laminæ of the colour of red iodide of mercury. On the spontaneous evaporation of its solution, ruby-red six-sided tables are formed, with angles of about  $110^\circ$ .

					Laurent.
32 C	.....	192	....	61.74	..... 61.90
3 N	.....	42	....	13.50	..... 13.45
13 H	.....	13	....	4.18	..... 4.40
8 O	.....	64	....	20.58	..... 20.25
<hr/>					
$C^{32}N^3H^{13}O^8$	.....	311	....	100.00	..... 100.00

*Decompositions.* 1. Isamic acid dissolves at first without decomposition in nitric acid, and imparts to it a violet colour, but the solution rapidly turns yellow. If the solution is heated with a little nitric acid till the violet colour has disappeared, a new body separates out on cooling which crystallises in microscopic needles, and is insoluble in water, but soluble in alcohol. — 2. The acid is decomposed by bromine, with formation of indelibrome, and of a yellow body which is soluble in alcohol and crystallises from the solution in nodules;—the latter body is insoluble in ammonia, but forms with potash a violet solution from which an orange yellow body is precipitated by acids. — 3. When boiled with dilute acids, it is converted into ammonia and isatin.

*Combinations.* Isamic acid is slightly soluble in boiling water and forms a yellow solution.

Strong sulphuric acid dissolves it, forming a beautiful violet-coloured solution, which turns yellow on the addition of water, and presently deposits isamic acid. The solution of the acid in small quantities of dilute sulphuric acid deposits violet needles on evaporation.

With hydrochloric acid it forms a beautiful violet solution, which on evaporation, yields violet needles turning red on the addition of water.

*Isamate of Ammonia* forms microscopic needles or very oblique rhombs. When dried at a strong heat, it loses 2 atoms of water and is converted into isamide.

*Isamate of Potash* is not decomposed by boiling with water.

*Isamate of Baryta* crystallises in yellow scales on evaporating a solution of the acid saturated with baryta. It contains 20.8 per cent. of baryta, corresponding to the formula  $C^{32}N^3H^{12}BaO^8$  (by calculation 20.2 per cent. BaO).

The ammonia-salt does not precipitate salts of lime and magnesia; with alum and acetate of lead it forms orange-yellow precipitates, with corrosive sublimate a red precipitate.

*Isamate of Silver* is obtained by precipitating the ammonia-salt with nitrate of silver.

				Laurent.	
32 C	.....	192	....	45.93	..... 48.0
3 N	.....	42	....	10.04	
12 H	.....	12	....	2.87	..... 2.9
Ag	.....	108	....	25.84	..... 24.5
8 O	.....	64	....	15.32	
<hr/>					
$C^{32}N^3H^{12}AgO^8$	.....	418	....	100.00	

Isamic acid is soluble in hot alcohol.

### Isamide.



LAURENT. (1841.) *N. Ann. Chim. Phys.* 3, 488; *J. pr. Chem.* 25, 460; *Pharm. Centr.* 1841, 261; *Rev. scient.* 18, 468; *J. pr. Chem.* 35, 117.

*Amasatin, Isamamide, Isaminamide.*

*Formation.* By heating isamate of ammonia :



*Preparation.* Isamate of ammonia, prepared according to 109, 2, is heated till water is evolved : and the residue is then washed with water. Laurent formerly obtained isamide in the following manner :— he filtered the mixture of imasatin and isamate of ammonia which is formed by treating isatin with aqueous or alcoholic ammonia, and evaporated the filtrate in order to drive off the ammonia and alcohol, whereupon a yellow precipitate was deposited ;— he then diluted with water, filtered, and decomposed the filtrate with the smallest possible quantity of hydrochloric acid ; washed the resulting red precipitate (consisting of isamic acid and isamide) on a filter with water ; and treated it with a little very dilute ammonia, by which the isamic acid was extracted.

*Properties.* Isamide forms a very beautiful yellow powder destitute of taste and odour.

				Laurent.	
32 C	.....	192	....	61.95	..... 61.74
4 N	.....	56	....	18.05	..... 17.90
14 H	.....	14	....	4.51	..... 4.52
6 O	.....	48	....	15.49	..... 15.84
<hr/>					
$C^{32}N^4H^{14}O^6$	.....	310	....	100.00	..... 100.00

*Decompositions.* 1. Isamide melts when heated, giving off water and ammonia, and leaves a residue which is completely soluble in potash ; at a stronger heat, vapours of a partly crystalline substance are evolved, and there remains a large residue of charcoal. — 2. It dissolves readily in cold nitric acid, and produces a violet solution, probably with formation of isamic acid. — 3. Dissolves very readily in sulphuric acid, with formation of isamic acid. — 4. Turns violet on the addition of concen-

trated hydrochloric acid; with dilute hydrochloric acid, it forms isamic acid in the cold, and isatin when heated. — 5. Treated with potash in the cold, it evolves ammonia and forms isamate of potash. — 6. When boiled for some time with water, it dissolves, a small quantity of ammonia being evolved and isamate of ammonia formed, while a small portion is converted into isatin and ammonia.

Isamide is insoluble in cold water and in ether; it is very slightly soluble in alcohol.

### Indelibrome.



LAURENT. (1842.) *Rev. scient.* 18, 472; *J. pr. Chem.* 35, 121.

*Formation and Preparation.* Isamic acid treated with bromine swells up violently and evolves hydrobromic acid; the excess of bromine is removed by alcohol or ether from the residue, which is then boiled with alcohol, thrown on a filter and washed.

*Properties.* Yellow powder, which melts when heated and crystallises in needles on cooling.

					Laurent.
32 C .....	192	...	35.50	.....	35.15
3 N .....	42	...	7.90	....	8.40
4 Br .....	320	...	43.30		
8 H .....	8	...	1.48	.....	1.47
8 O .....	64	...	11.82		
<hr/>					
$C^{32}N^3Br^4H^8O^8$ .....	626	...	100.00		

It sublimes when heated in a tube, but the greater part is decomposed. Ammonia and potash, even when boiling, are without action upon it. It is also not decomposed by concentrated hydrochloric acid.

### Chlorisamic Acid.

LAURENT. (1842.) *Rev. scient.* 18, 464; *J. pr. Chem.* 25, 462.

*Formation and Preparation.* Sulphate of ammonia is added to the alcoholic solution of chlorisatate of potash; the precipitate of sulphate of potash is filtered off; the filtrate is evaporated till it forms a doughy mass, which is treated with dilute potash; the solution is decomposed by hydrochloric acid, not in excess; and the precipitated red flakes are recrystallised from alcohol.

*Properties.* Very similar to isamic acid; forms brilliant red, microscopic rhombic or six-sided prisms, with angles of about  $110^\circ$ .

					Laurent.
32 C	.....	192	...	50.55	..... 50.00
3 N	.....	42	...	11.05	
2 Cl	.....	70.8	...	18.65	
11 H	.....	11	...	2.90	..... 2.96
8 O	.....	64	...	16.85	
<hr/>					
$C^{32}N^3Cl^2H^{11}O^8$ .....					379.8 .... 100.00

Decomposed by distillation. — Forms violet-coloured solutions with concentrated acids. By boiling with acids it is converted into ammonia and chlorisatin. The ammonia-salt evaporated to dryness yields chlorisamide.

The ammonia-salt forms a yellow precipitate with salts of silver.

Chlorisamic acid is more readily soluble in alcohol and in ether than isamic acid, and forms yellow solutions.

### Chlorisamide.



LAURENT. *J. pr. Chem.* 25, 462.

#### Chlorisamamide.

Obtained as a yellow powder by evaporating aqueous chlorisamate of ammonia.

					Laurent.
32 C	.....	192	...	50.70	
4 N	.....	56	...	14.80	
2 Cl	.....	70.8	...	18.70	..... 18.08
12 H	.....	12	...	3.15	
6 O	.....	48	...	12.65	
<hr/>					
$C^{32}N^4Cl^2H^{12}O^8$ .....					378.8 .... 100.00

Concentrated acids dissolve it with violet colour; cold dilute acids convert it into chlorisamic acid, and at the boiling heat into chlorisatin.

It is insoluble in *boiling water*.

### Bichlorisamic Acid.



LAURENT. *J. pr. Chem.* 25, 462.

On boiling bichlorisamide with alcohol, a solution of bichlorisamate of ammonia is obtained, which forms yellow flakes with nitrate of silver; the precipitate turns violet on the addition of hydrochloric acid and yields 26 per cent. of chloride of silver. (The calculated quantity is 26.6 per cent. AgCl.)

**Bichlorisamide.**LAURENT. *J. pr. Chem.* 25, 462.*Bichlorisamamide.*

When an alcoholic solution of bichlorisatate of potash is mixed with sulphate of ammonia and the filtrate is evaporated, bichlorisamide separates as a yellow powder, which is converted into bichlorisamate of ammonia by boiling with alcohol.

**Isatylim.**LAURENT. (1842.) *Rev. scient.* 18, 472; *J. pr. Chem.* 35, 121.

*Formation and Preparation.* When the mother-liquor obtained in the preparation of isatimide is decanted from the last deposits of isatimide and imasatin, and gently evaporated on a sand-bath, it suddenly becomes filled with light yellow flakes; and if these are immediately filtered off, washed with a little alcohol and dissolved in boiling alcohol; isatylim separates out on cooling in yellow amorphous flakes.

					Laurent.
48 C	.....	288	...	65.55	..... 65.33
4 N	.....	56	...	12.71	..... 13.00
16 H	.....	16	...	3.64	..... 3.76
10 O	.....	80	...	18.10	..... 17.91
<hr/>					
C <sup>48</sup> N <sup>4</sup> H <sup>16</sup> O <sup>10</sup>	.....	440	...	100.00	..... 100.00

Isatylim does not turn violet when treated with concentrated hydrochloric acid, but dissolves in the acid with yellow colour on the addition of alcohol; the solution does not deposit isatin on cooling. — It is readily soluble in potash, from which it is precipitated in yellow flakes by acids.

The alcoholic solution produces a reddish yellow precipitate with nitrate of silver.

**Isatimide.**LAURENT. *J. pr. Chem.* 35, 121.

*Formation and Preparation.* Isatin is gently warmed with a quantity of alcohol not sufficient to dissolve the whole of it, at the boiling heat; dry gaseous ammonia is then passed through till all the isatin is dissolved.

If absolute alcohol is used, imasatin first crystallises from the solution in rectangular prisms, and the solution decanted therefrom deposits isatimide as a yellow crystalline powder. The liquid decanted from the last product and evaporated, yields a little more isatimide mixed with brown grains and imasatin. In order to purify the isatimide from any imasatin it may contain, it is boiled with alcohol containing a little ammonia, in which the isatimide dissolves; it is then deposited from the filtrate in crystals on cooling.

*Properties.* Yellow rhombic tables insoluble in water.

				Laurent.
48 C	.....	288	... 65.61	..... 65.5
5 N	.....	70	... 16.06	..... 16.1
17 H	.....	17	... 3.87	..... 4.0
8 O	.....	64	... 14.46	..... 14.4
<hr/>				
$C^{48}N^5H^{17}O^8$	.....	439	... 100.00	..... 100.0

*Decompositions.* 1. Melts and turns brown when heated. Dissolves in potash with evolution of ammonia, and forms a yellow solution, from which hydrochloric acid precipitates yellow flakes soluble in alcohol; the alcoholic solution yields on evaporation a mixture of isatin and rounded crystalline grains. — 2. It dissolves in a boiling mixture of hydrochloric acid and alcohol; bichloride of platinum precipitates chloroplatinate of ammonium from the solution. — (The nitrogen contained in it amounts to one-fourth only of the nitrogen which has been added to the isatin by the action of ammonia.) — The supernatant liquid contains isatin together with a blue and a resinous substance.

### Amisatin.



LAURENT. *J. pr. Chem.* 35, 121.

When the mother-liquor from the preparation of isatolim is mixed with hot water, a white resinous precipitate is formed; and the filtrate yields a purple-red crystalline precipitate, which is boiled with alcohol containing a little potash. The hot solution is neutralised with hydrochloric acid, and the amisatin which separates out cooling, is washed with alcohol.

Short, slender, microscopic needles.

				Laurent.
96 C	.....	576	... 63.12	..... 62.60
11 N	.....	154	... 16.80	..... 16.80
39 H	.....	89	... 4.26	..... 4.05
18 O	.....	144	... 15.82	..... 16.55
<hr/>				
$C^{96}N^{11}H^{39}O^{18}$	.....	913	... 100.00	..... 100.00

Amisatin is insoluble in alcohol.

**Bibromocarmindin.**

LAURENT. (1842.) *Rev. scient.* 18, 478; *J. pr. Chem.* 35, 127.

*Formation and Preparation.* 1. When bromisatin is gently heated with alcohol and a small quantity of ammonia in a flask placed on a sand-bath, the bromisatin dissolves, and after 10 or 15 minutes, the yellow solution gradually assumes a rose-red colour, while bibromisatin separates out. As soon as the rose-colour has become intense, the liquid is decanted or filtered, water is then added, and the carmine-coloured precipitate thereby produced is separated by filtration. The liquid runs through very slowly; the filtration may indeed be accelerated by neutralising with an acid: but the bibromocarmindin then becomes contaminated with a yellow body. The substance on the filter is dissolved in ether and the filtered solution is added by drops to a mixture of ether and alcohol; the bibromocarmindin then separates out as the ether evaporates. — 2. Bibromisatate of ammonia is dried at a strong heat, and the residue is exhausted with ether.

*Properties.* Of a deep rose-red colour like the finest carmine.

					Laurent.
64 C .....	384	...	31.55	.....	31.10
7 N .....	98	...	8.05	.....	8.20
8 Br .....	640	...	52.23		
15 H .....	15	...	1.23	.....	1.65
10 O .....	80	...	6.94		
<hr/> $C^{64}N^7Br^8H^{15}O^{10}$ ....1217					100.00

Bibromocarmindin is converted by hydrochloric acid into a yellow powder. It dissolves in alcohol containing potash, forming a red solution which afterwards turns yellow. Acids precipitate from this solution a yellow body soluble in ether. Bibromocarmindin does not dissolve in caustic potash or in ammonia.

It is sparingly soluble in alcohol, and dissolves very freely in ether, forming a rose-coloured liquid.

**XYLENE SERIES.****A. PRIMARY SERIES.****PRIMARY NUCLEUS  $C^{16}H^{10}$ .****Xylol  $C^{16}H^{10}$ .**

CANOURS. (1850.) *Compt. rend.* 30, 319; also *Ann. Pharm.* 74, 168; 76, 286.

VÖLCKEL. *Ann. Pharm.* 86, 109, 334; also *N. Ann. Chim. Phys.* 41, 488.

A. H. CHURCH. *Phil. Mag. J.* [4] 9, 256; also *J. pr. Chem.* 67, 43; *Gerh. Traité* 4, 1031.

H. KOPP. *Ann. Pharm.* 96, 29.

*Xylene.* (Cahours, Völckel.)

*Formation.* 1. In the dry distillation of wood, passing into the crude wood-spirit (Cahours, Church), and the light tar-oil. (Völckel.) — 2. In the dry distillation of coal: it is found in coal-tar-oil. (Church.)

*Preparation.* 1. The portion which passes over from 128° to 130°, after the toluol, in the distillation of wood-spirit treated according to vi. 175, is xylol. (Cahours, Church.) — 2. That portion of the light oil of tar from beechwood, passing over between 130° and 150°, is for the most part soluble in oil of vitriol; the undissolved part begins to boil at 110°. From 130° to 150° xylol distils over. (Völckel.) — 3. The portion of coal-tar-oil which passes over near 128° is treated successively with hydrate of potash, oil of vitriol, an aqueous solution of chromic acid, caustic baryta, and sodium, whereby the boiling point is reduced to 126·2°. (Church.)

*Properties.* Colourless oil, having an odour similar to that of benzol, and a burning taste (Völckel); much resembling toluol in its properties. (Cahours.) Boils at 128°—130° (Cahours), at 126·2°, under a pressure of 0·76 met. (Church.)

					Völckel.
16 C .....	96	...	90·56	.....	90·53
10 H .....	10	...	9·44	.....	9·48
<hr/>					
C <sup>16</sup> H <sup>10</sup> .....	106	...	100·00	.....	100·01

The vapour-density corresponds with this formula. (Cahours.)

*Decompositions.* 1. Xylol burns with a fuliginous flame. (Völckel.) — 2. Concentrated *nitric acid* colours xylol yellow, and, when heated, dissolves it with evolution of red fumes. Water separates from this solution a heavy yellow oil. (Völckel.) Distilled with fuming nitric acid it yields nitroxylol and binitroxylol. (Cahours.) Cold nitric acid of sp. gr. 1·5 forms nitroxylol. (Church.) — 3. *Oil of vitriol*, in contact with xylol for some time, gradually dissolves it. (Völckel.) Xylol kept in contact for a week with fuming oil of vitriol, forms sulphoxylic acid. (Church.)

*Combinations.* Xylol is insoluble in water, readily soluble in alcohol and ether. (Völckel.)

### Sulphoxylic Acid.



CHURCH. *Phil. Mag. J.* [4] 9, 453; also *J. pr. Chem.* 67, 43; *Gerh. Traité* 4, 1031.

*Acide xylenylsulfureux, Xylol-schwefelsäure.*

*Formation.* From xylol and fuming sulphuric acid (vi, 482.)



*Preparation.* Xylol is mixed with 4 vol. of fuming sulphuric acid, the mixture set aside for a week, and the separated crystals dried over sulphuric acid. The reddish-yellow mother-liquor containing an excess of sulphuric acid, when neutralised with carbonate of baryta and filtered from the sulphate of baryta, yields, on evaporation, sulphonylolate of baryta.

*Properties.* Colourless shining tufts of crystals, which melt without decomposition in vacuo or in xylol-vapour, and solidify on cooling in delicate needles having an acid, and afterwards a bitter taste. Has a strong acid reaction.

*Decompositions.* When heated above its melting point, it becomes black.

*Combinations.* Crystallises well from xylol; dissolves readily in water and in oil of vitriol.

*Sulphonylolate of Baryta* crystallises in transparent scales similar to sulphotolulate of baryta. The hot concentrated solution, mixed with cold water, deposits the salt in beautiful iridescent scales. The solution is not decomposed by boiling.

					Church.
Ba .....	68.6	....	27.05	.....	26.97
$C^{16}H^9S^2O^6$ .....	185	....	72.95		
<hr/>					
$C^{16}H^9BaS^2O^6$ ....	253.6	....	100.00		

### Terebentic Acid.



PERSONNE. *Compt. rend.* 48, 553; *Ann. Pharm.* 100, 253.

*Preparation.* The vapours of terpin are passed over soda-lime heated to  $400^\circ$ , and the product is treated with hydrochloric acid. Marsh-gas and hydrogen are thereby disengaged :



*Properties.* Solid, white. When obtained by cooling the hot saturated solution, it forms a white powder composed of needles. When sublimed it crystallises in small scales, which appear to be oblique prisms. Has a faint but rank odour. Denser than water. Melts at  $90^\circ$ , boils at  $250^\circ$ . The vapour is acrid and irritates the nose strongly.

*Decompositions.* The acid appears to decompose to a slight extent during distillation.

*Combinations.* It is nearly insoluble in cold water, but dissolves more readily in boiling water.

*Terebentilate of Lime*, obtained by combining the acid with lime, forms small, white, silky needles, resembling sulphate of quinine.

				Personne.
CaO .....	28	...	17.83	..... 17.68
C <sup>16</sup> H <sup>9</sup> O <sup>3</sup> .....	129	...	82.17	
<hr/>				
C <sup>16</sup> H <sup>9</sup> CaO <sup>4</sup> .....	157	...	100.00	

*Terebentilate of Lead* does not crystallise, and when dry resembles gum-arabic.

*Terebentilate of Silver*. — Sparingly soluble in boiling water; crystallises on cooling.

				Personne.
16 C .....	96	...	39.18	..... 38.92
9 H .....	9	...	3.67	..... 3.70
Ag .....	108	...	44.08	..... 43.90
4 O .....	32	...	13.07	..... 13.48
<hr/>				
C <sup>16</sup> H <sup>9</sup> AgO <sup>4</sup> .....	245	...	100.00	..... 100.00

Terebentilic acid is very easily soluble in alcohol.

With alcohol it readily forms an ether, having the odour of pears and pine-apples.

It is readily soluble in ether.

### *Secondary-nuclei of Xylene.*

*Oxygen-nucleus* C<sup>16</sup>H<sup>9</sup>O<sup>3</sup>. *Anisene*.

### **Anisalcohol,**



S. CANNIZARO u. C. BERTAGNINI. (1856.) *Nuovo Cimento* 1, 99; *Ann. Pharm.* 98, 188; *J. pr. Chem.* 68, 445; *Pharm. Centr.* 1856, 505.

*Formation and Preparation.* When anisylous acid is dissolved in an equal volume of alcohol, and the liquid is mixed with three times its volume of an alcoholic solution of potash of 7°Bm., the mixture solidifies, with slight evolution of heat, into a crystalline mass. After 10 to 12 hours, the alcohol is distilled off in the water-bath, the residue is suspended in water, and the anisalcohol extracted from the liquid by ether. On distilling the brown oil left after evaporation of the ether, anisalcohol passes over at 260° as a colourless liquid crystallising at a low temperature. If it contains, as it generally does, unaltered anisylous acid (recognisable by the formation of crystals when shaken with an aqueous solution of an alkaline bisulphite), it is once more treated with a little alcoholic potash, rectified in a stream of carbonic acid, and the solidified distillate is pressed between blotting paper.

*Properties.* Hard, white, shining needles, melting at about  $23^\circ$ , but when moist at a lower temperature, even as low as  $7^\circ$ . Denser than water. Boils at  $248^\circ - 250^\circ$ . Has a faintly alcoholic and sweetish odour, and burning taste, recalling that of oil of anise.

Cannizaro & Bertagnini.				
mean.				
16 C .....	96	....	69.56	..... 69.41
10 H .....	10	....	7.24	..... 7.33
4 O .....	32	....	23.20	..... 23.26
<hr/>				
$B^{16}H^{10}O^4$ .....	138	....	100.00	..... 100.00

*Decompositions.* 1. Does not change when exposed to the air at ordinary temperatures, but when heated near its boiling point, it absorbs oxygen and is converted into anisylous acid. — 2. Oxidising agents transform it first into anisylous acid, and then into anisic acid. Evolves with platinum-black, the odour of anisylous acid, and after several days is transformed into anisic acid. Hot nitric acid has the same effect. — 3. With moderately concentrated *sulphuric acid*, it forms a reddish resinous mass. — 4. Anhydrous *phosphoric acid* acts like oil of vitriol.

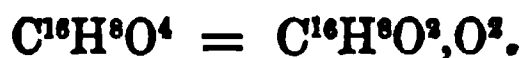
5. When anisalcohol is moderately heated with *chloride of zinc*, a violent action ensues; water is formed which combines with the chloride of zinc; and above it floats an oily layer, which, on cooling, solidifies into a hard, transparent, vitreous mass, insoluble in water and alcohol, soluble in bisulphide of carbon, and melting only at a temperature of  $100^\circ$ .

6. *Hydrochloric Acid gas* is absorbed by anisalcohol with evolution of heat, the fluid becoming turbid and separating into two layers, the lower of which contains aqueous hydrochloric acid, and the upper seems to be hydrochlorate of anisene (p. 131).

7. *Potassium* dissolves in liquid anisalcohol with evolution of hydrogen—which is violent if heat is applied—and forms a yellow liquid, which solidifies like butter on cooling.

*Combinations.* Anisalcohol, when hot, dissolves several salts, as benzoate, anisate, and acetate of potash, which crystallise from it on cooling. It dissolves salicin, phillyrin, hippuric acid, and other organic substances.

### Anisylous Acid.



CAHOURS. (1844.) *Compt. rend.* 19, 795; *N. Ann. Chim. Phys.* 14, 483; 23, 354; *J. pr. Chem.* 36, 422; abstr. *Ann. Pharm.* 56, 307; *Compt. rend.* 25, 458.

BERTAGNINI. *Ann. Pharm.* 85, 268.

CANNIZARO & BERTAGNINI. *Ann. Pharm.* 98, 189.

PIRIA. *Nuovo Cimento.* 3, 126; *N. Ann. Chim. Phys.* 48, 114; *Ann. Pharm.* 100, 104.

*Hydruret of anisyl, Anisylwasserstoff, Anisaldehyd, Hydrure d'anisyle.*

*Formation.* In the oxidation of anisalcohol by the oxygen of the air or by nitric acid. (Cannizaro & Bertagnini.) — 2. When oil of anise

is heated with dilute nitric acid, oxalic acid and carbonic acid being formed at the same time. (Cahours.)—3. In the distillation of anisate of lime with formiate of lime, carbonate of lime remaining behind. (Piria.)



*Preparation.* Stearoptene of oil of anise is heated with dilute nitric acid, and the indifferent reddish oil which is first formed, and resembles a thick fatty oil when cold, is washed repeatedly with water and distilled at the lowest possible temperature, a small quantity of charcoal then remaining behind. The distillate is composed of crystallised anisic acid and a heavy reddish oil consisting of anisyulous acid. From this mixture the anisic acid is extracted by dilute aqueous potash. The oil repeatedly washed with water, and two or three times carefully rectified, yields pure anisyulous acid, which may be obtained colourless by repeated distillation in a stream of carbonic acid gas. (Cahours.)

2. Oil of anise is boiled for an hour with 3 vol. of dilute nitric acid of 14° Bm.; and the oily product is washed with water, then with a dilute solution of potash, and distilled. The distillate, shaken with a warm solution of bisulphite of soda of 30° Bm., yields, on cooling, crystals of the compound of anisyulous acid with bisulphite of soda, which are washed with alcohol till the washings no longer render water turbid, then dissolved in a little hot water, and heated with aqueous carbonate of potash, whereby anisyulous acid is separated, which must be purified from adhering salt by distillation. (Cannizaro & Bertagnini.)

*Properties.* Colourless or slightly yellow oil. Boils between 253° and 255°. Sp. gr. 1.09 at 20°. Has an aromatic odour like that of hay, and a burning taste. (Cahours.)

					Cahours. mean.
16 C .....	96	...	70.59	.....	70.44
8 H .....	8	...	5.88	.....	6.11
4 O .....	32	...	23.53	.....	23.45
<hr/>					
$\text{C}^{16}\text{H}^8\text{O}^4$ .....	136	...	100.00	.....	100.00

Bears the same relation to anisic acid as salicyulous acid to salicylic acid. (Cahours.)

*Decompositions.* 1. The acid acquires a darker colour by keeping. — 2. When exposed to the air, it absorbs oxygen and is converted slowly but completely, into anisic acid. — 3. It is transformed into anisic acid by boiling with dilute *nitric acid*. Forms a crystallisable product with fuming nitric acid. — 4. With *bromine* it becomes heated, evolving much hydrobromic acid, and yields crystallised bromanisyl. — 5. *Chlorine* acts like bromine, forming hydrochloric acid and chloranisyl. — 6. Anisyulous acid is violently acted upon by *pentachloride of phosphorus*, evolving much hydrochloric acid, yielding a small quantity of liquid products, viz., chlorophosphoric acid and a neutral oil which smells strongly of oil of turpentine, and leaving a black pitchy mass.

7. Anisyulous acid left for some time in contact with *ammonia* forms anishydramide. — 8. The alcoholic solution, mixed with *sulphide of ammonium* yields thianisiol. (Cahours.)

8. Anisylous acid does not dissolve in cold *aqueous potash*; by access of air, anisate of potash is formed; when boiled with potash, it is completely dissolved. When anisylous acid is dropped on fused hydrate of potash, hydrogen is evolved and anisate of potash formed, every drop forming a sort of vegetation; the whole is ultimately converted into a doughy mass. (Cahours.)—With alcoholic potash, anisylous acid is resolved into anisalcohol and anisate of potash (p. 119). (Cannizaro & Bertagnini.)

*Combinations.* Anisylous acid is but slightly soluble in *water*, to which it imparts its odour. It dissolves in cold *oil of vitriol* with dark red colour, and is reprecipitated by water. (Cahours.)

With *Bisulphite of Ammonia*. — Anisylous acid shaken up with aqueous bisulphite of ammonia, becomes heated and immediately forms a crystalline product, which is easily soluble in water and insoluble in aqueous sulphites. (Bertagnini.)

With *Bisulphite of Potash*. — Anisylous acid shaken up with a solution of bisulphite of potash, forms a buttery, and afterwards crystalline mass, which, when the mother-liquor has run off, may be recrystallised from dilute alcohol.

It is easily resolved into anisylous acid and sulphite of potash. May be exposed to the air for a long time without perceptible alteration. Dissolves readily in water, and is reprecipitated by cold saturated solutions of sulphites. (Bertagnini.)

With *Bisulphite of Soda*. — 1. Obtained like the potash-compound. — 2. The heavy reddish oil formed by dilute nitric acid from oil of anise (p. 121) is digested with a warm dilute solution of bisulphite of soda. The solution becomes filled with granular crystals on cooling.

Colourless shining scales. Prepared according to 2, it forms crystalline nodules.

					Bertagnini.
NaO .....	31	...	12.91	.....	12.94
16 C .....	96	...	40.00	.....	39.28
9 H .....	9	...	3.75	.....	3.84
2 S .....	32	...	13.33	.....	13.76
9 O .....	72	...	30.01	.....	30.18
$C^{16}H^8O^4 + NaO, 2SO^2 + Aq$ .....					240 ... 100.00 ..... 100.00

When heated it evolves sulphurous and anisylous acid. The aqueous solution becomes turbid when slightly heated, and yields anisylous acid on boiling. If the water contains sulphite of soda, the solution may be heated without any separation of anisylous acid taking place.

The compound is decomposed by acids and alkalis into sulphurous acid and anisylous acid; by nitric acid, into sulphuric acid and anisylous acid. Iodine and bromine act like nitric acid; bromine in excess forms soft white needles, which melt in boiling water and form a crystallisable compound with bisulphite of soda, probably bromanisylous acid. Ammonia dissolves the compound of anisylous acid with bisulphite of soda, separating an oily substance which crystallises after a while and has the properties of anishydramide.

It dissolves in cold water, less in water containing a little sulphite of soda. It is nearly insoluble in a cold saturated solution of sulphite of soda. Soluble in alcohol. (Bertagnini.)

Anisylous acid mixes with alcohol and ether in all proportions. (Cahours.)

### Anisic Acid.



CAHOURS. *Rev. scient.* No. 9, Sept. 1840, 342; *J. pr. Chem.* 22, 58; *N. Ann. Chim. Phys.* 2, 287; *J. pr. Chem.* 24, 348; *Ann. Pharm.* 41, 66; *Compt. rend.* 15, 804; *N. Ann. Chim. Phys.* 10, 327; *Compt. rend.* 19, 795; *N. Ann. Chim. Phys.* 14, 489; *J. pr. Chem.* 36, 421; *N. Ann. Chim. Phys.* 23, 351; 25, 1; *Ann. Pharm.* 69, 236; *N. Ann. Chim. Phys.* 27, 439; *Ann. Pharm.* 74, 298.

WELTZIEN. *J. pr. Chem.* 22, 197.

LAURENT. *Rev. scient.* 10, 5; *J. pr. Chem.* 27, 232; *Rev. scient.* 10, 362; 11, 258; 14, 565; *Compt. rend.* 15, 744, 953.

PERSOZ. *Compt. rend.* 13, 438; *J. pr. Chem.* 25, 55; *Ann. Pharm.* 44, 311.

GERHARDT. *Compt. rend.* 15, 498; *N. Ann. Chim. Phys.* 7, 292.

BERZELIUS. *Jahresber.* 23, 420.

HEMPEL. *Ann. Pharm.* 59, 104.

BERTAGNINI. *Ann. Pharm.* 97, 252.

CANNIZARO & BERTAGNINI. *Ann. Pharm.* 98, 189.

L. ZERVAS. *Ann. Pharm.* 103, 339; *Pharm. Centr.* 1858.

*Anistinsäure, Anisylsäure, Acide anisique, draconique, dracique, ombellique, badianique.*

Cahours, in 1839, obtained anisic acid from oil of anise, and assigned to it the formula  $C^{10}H^7O^6$ . Laurent, in 1841, prepared from the oil of *Artemisia dracunculus*, an acid which he called *Acide draconique*, and whose formula he gave as  $C^{10}H^{11}O^6$ . Gerhardt showed that the two were identical, and contain  $C^{10}H^8O^6$ . Persoz, in 1841, obtained the same acid from oil of star-anise and oil of fennel, and called it *Acide ombellique* and *badianique*, although Cahours had already shown that the solid part of these oils has the same composition as that of oil of anise. Hempel established the identity between Persoz's *Acide badianique* and anisic acid.

*Formation.* 1. From anisalcohol by oxidation (p. 120). (Cannizaro & Bertagnini.) — 2. From anisylous acid by oxidation in the air or by means of nitric acid, by fusing with hydrate of potash, or by boiling with a solution of potash with access of air (p. 121). (Cahours.) — 3. From anise-camphor (stearoptene of oil of anise, the solid part of the volatile oils of *Pimpinella anisum*, *Anethum feniculum* and *Illicium anisatum*) by oxidation with nitric acid (Cahours, Weltzien); or with aqueous chromic acid. (Persoz, Hempel.) — 4. From the volatile oil of *Artemisia dracunculus* by oxidation with nitric acid. (Laurent.) — 5. From Carajuru or Chica (a red colouring matter extracted from the leaves of the *Bignonia chica*,

a South American plant), by oxidation with heated nitric acid, or with dilute chromic acid. (Erdmann, *J. pr. Chem.* 71, 198.)

*Preparation.* 1. Anise-camphor is treated with nitric acid of  $23^\circ$  or  $24^\circ$ ; the liquid, after being freed from a yellow resin, is poured off from the crystals, which are washed with cold water and dissolved in ammonia; the ammonia-salt is purified by repeated crystallisation, and precipitated by neutral acetate of lead; the precipitate, which is but slightly soluble in water, is washed with water and decomposed by hydrosulphuric acid; the free anisic acid is extracted by boiling water; and the crystals which are obtained on cooling are purified by sublimation. (Cahours.) — 2. *Oil of tarragon* is introduced into a capacious retort together with water, heat is applied, and three times the quantity of common nitric acid gradually added. The oil becomes steadily thicker, swells up very much, and at last solidifies completely to a brown, somewhat crystalline, resinous mass. This mass is freed from nitric acid by water, and boiled with an excess of dilute ammonia, which almost entirely dissolves it, leaving only a slight brown residue, which may again be treated with nitric acid. The brownish-red ammoniacal solution holds anisic acid and nitranisic acid in solution, together with a brown resin. To remove this, the solution is evaporated to the consistence of syrup, whereby the ammonia in which the brown resin is dissolved is expelled (if the evaporation is carried too far, the acids also lose some of their ammonia and remain behind with the resin; the residue must then be redissolved in ammonia and once more evaporated); the syrup is dissolved in water; the liquid is filtered, and again evaporated; and the residue is redissolved in water to get rid of the remains of the brown resin, which is at last totally removed by means of animal charcoal. On evaporating the solution, anisate of ammonia crystallises in rhombic plates (if needles of anisic acid are obtained instead, a little ammonia must be added), which are recrystallised from alcohol, dissolved in hot alcohol and water, and while hot decomposed with nitric acid. On cooling, anisic acid crystallises in needles, which are obtained of a brilliant white by recrystallisation from alcohol, distillation, and recrystallisation of the distillate. (Laurent.) — 3. Fifty or sixty grammes of *oil of anise*, *star-anise*, or *fennel*, distilled with a mixture of 500 gr. of bichromate of potash, 1100 gr. oil of vitriol, and 4000 gr. water, yield acetic acid and an insoluble product, which is a mixture of two acids: *ombellic* and *badianic acid*. (Persoz.) With 30 gr. fennel-oil, an exceedingly violent action of short duration takes place. The liquid, when cold, is filtered, and the residue is washed and boiled in a retort with carbonate of potash; unaltered oil then collects in the receiver, together with acetic acid smelling of camphor. The filtered residue precipitated with nitric acid, washed, dissolved in boiling alcohol, which leaves but little camphor on the filter (real camphor seems to be understood. Gm.), decolorised with charcoal and filtered while hot, yields, on cooling, colourless needles of anisic acid, from which ether does not extract any badianic acid. (Hempel.) 6 pts. of bichromate of potash are dissolved in a capacious vessel in 9 pts. water, 7 pts. sulphuric acid are added, and, whilst the liquid is stirred, 1 pt. of oil of anise. A violent action, attended with frothing, then commences after a while. After half an hour, cold water is added to separate the anisic acid, which is purified by recrystallisation from hot alcohol. The product amounts to 50 p. c. (Zervas.)

*Properties.* Anisic acid crystallises from hot water in long, brilliant,



colourless (rhombic, Persoz), needles. (Cahours.) From alcohol it crystallises in shining rhombic prisms one or two inches long, with angles of  $114^\circ$  and  $66^\circ$ . The sharp edges are mostly truncated; the base is replaced by two principal faces and three smaller ones. (Laurent.) Melts at  $175^\circ$  (Laurent), at  $175^\circ - 180^\circ$  (Persoz); and on cooling congeals into a mass of needles. (Laurent.) While the melted acid is solidifying, numerous small bubbles are evolved from the still liquid part, which for the most part burst on the surface. (Persoz.) The acid may be volatilised and distilled at a higher temperature without decomposition. (Cahours, Laurent.) Boils at  $275^\circ - 280^\circ$ , but sublimes even at a lower temperature. (Persoz.) Inodorous; has a scarcely perceptible taste. The solutions redden litmus. Permanent in the air. (Laurent.)

Cahours.							
				a.	b.		
16 C	.....	96	...	63.15	.....	63.46	... 63.18
8 H	.....	8	...	5.26	.....	4.71	... 5.19
6 O	.....	48	...	31.59	.....	31.83	... 31.63
<hr/>							
$C^{16}H^8O^6$	.....	152	...	100.00	.....	100.00	... 100.00

				Laurent.	Hempel.		Bertagnini.
				a.	b.		
16 C	.....	96	.....	62.92	...	62.83	... 63.16
8 H	.....	8	.....	5.22	... 5.30	5.36	... 5.42
6 O	.....	48	.....	31.86	...	31.81	... 31.42
<hr/>							
$C^{16}H^8O^6$	.....	152	.....	100.00	...	100.00	... 100.00

Isomeric with methylsalicylic acid and formobenzollic acid.

Cahours examined the acid from stearoptene of oil of anise (*a*), and from anisylous acid (*b*); Laurent, the acid from oil of tarragon (*a*), and later that from oil of anise (*b*), Hempel's acid was obtained from oil of fennel with chromic acid; Bertagnini's from urine after anisic acid had been swallowed.

*Decompositions.* 1. Burns easily, and with a somewhat fuliginous flame, when heated on platinum-foil. — 2. *Bromine* converts it into bromanisic acid. — 3. When *chlorine* is passed through melted anisic acid, hydrochloric acid and chloranisic acid are formed. (Laurent.) — 4. *Pentachloride of phosphorus* acts violently on anisic acid, forming hydrochloric acid, chlorophosphoric acid, and chloranisyl. (Cahours.) — 5. Digested with *fuming sulphuric acid*, or heated with oil of vitriol to  $110^\circ$ , it yields sulphanisic acid. (Zervas.) Anisic acid, heated with fuming sulphuric acid to  $140^\circ - 200^\circ$ , forms bisulphanisic acid, with evolution of carbonic acid :



If it were heated to a higher degree, sulphurous acid and other products would be formed. (Zervas.) — 6. It dissolves in concentrated *nitric acid*, forming a compound analogous to nitrobenzoic acid. (Weltzien.) With nitric acid it forms nitranisic and binitranisic acid. (Laurent.) Anisic acid dissolves in fuming nitric acid at a gentle heat, yielding nitranisic acid, precipitated by water; on boiling the solution, carbonic acid is disengaged, and, according to the time for which the action continues or the proportions of the substances employed, binitranisol or ternitranisol is formed, frequently also chryanisic acid, and lastly picric acid. (Cahours.)



—7. *Nitrosulphuric acid* dissolves anisic acid readily at a gentle heat. and when more strongly heated forms ternitranisol (xii, 265) with disengagement of a gas containing carbonic acid. (Cahours.) — 8. Distilled with excess of *baryta*, it yields anisol. (Cahours, Laurent.) — 9. Taken internally, it passes unaltered into the urine. (Bertaguini.)

*Combinations.* Anisic acid is scarcely soluble in cold, but dissolves somewhat freely in boiling water, from which it crystallises on cooling.

*Salts of Anisic Acid: Anisates.* — Anisic acid yields, with the alkalies, alkaline earths, and earths proper, soluble and crystallisable salts.

*Anisate of Ammonia.* — Plates derived from a right rhombic prism, with lateral edges of  $84^\circ$  and  $96^\circ$ ; the edges of the base are truncated by faces which are inclined to each other at  $164^\circ 30'$ . The acute lateral edges are mostly truncated. In vacuo at  $80^\circ$  to  $99^\circ$ , the crystals lose 10.8 p. c., and leave anisic acid. (Laurent.) Anisic acid dissolves readily in cold ammonia, the solution yielding by spontaneous evaporation, fine large cubes resembling common salt. The crystals become opaque by exposure to the air. (Cahours.)

					Laurent.
$C^{16}H^8O^6$	.....	152	...	89.95	
$NH^3$	.....	17	...	10.05	..... 10.8
<hr/>					
$C^{16}H^6NH^4O^6$	.....	169	...	100.00	

The salt is resolved by heat into ammonia and anisic acid, which then shows a somewhat higher melting point. (Pisani, *Compt. rend.* 44, 838.)

*Anisate of Potash* crystallises in rhombic or in six-sided plates; the soda-salt in needles. (Laurent.) Anisate of potash dissolves in anis-alcohol. (Cannizzaro & Bertagnini.)

*Anisate of Baryta.* — Chloride of barium does not at first precipitate anisate of ammonia, but after several minutes rhombic scales are formed. When hydrate of baryta is boiled with the acid and with water, the hot filtrate yields, on cooling, first needles and then rhombic scales. (Laurent.)

					Laurent.
$C^{16}H^7O^6$	.....	143	...	62.55	
$BaO$	.....	76.6	...	33.50	..... 34.63
$HO$	.....	9	...	3.95	
<hr/>					
$C^{16}H^7BaO^6 + Aq$	....	228.6	...	100.00	

*Anisate of Strontia.* — Chloride of strontium does not at first precipitate anisate of ammonia, but after some time six-sided or rectangular plates are formed. (Laurent.)

*Anisate of Lime.* — Anisate of ammonia immediately precipitates chloride of calcium. When the mixture is sufficiently diluted, it first yields fine needles and afterwards rectangular plates. (Laurent.)

*Anisate of Ammonia* produces no precipitate with solution of sulphate of *magnesia*; with dilute solution of *alum*, shining needles are slowly formed.

With protosulphate of *manganese*, small crystals are gradually formed. Sulphate of *zinc* is precipitated white. (Laurent.)

*Anisate of Lead* crystallises from the boiling aqueous solution on cooling in pearly scales, which are but slightly soluble in cold water. (Cahours.) *Anisate of ammonia*, mixed warm with acetate of lead, produces microscopic needles. (Laurent.)

				Cahours.	
				<i>in vacuo at 120°.</i>	
16 C.....	96	....	37.68	.....	36.43
7 H.....	7	....	2.75	.....	2.77
5 O.....	40	....	15.69		
PbO .....	111.8	....	43.88		
<hr/>					
C <sup>16</sup> H <sup>7</sup> PbO <sup>6</sup> .....	254.8	....	100.00		

Cahours at first adopted the formula C<sup>16</sup>H<sup>7</sup>PbO<sup>7</sup>.

Anisic acid precipitates the *sesqui-salts of iron*, but not the proto-salts. (Cahours.) *Anisate of ammonia* gives, with sesquichloride of iron, a yellow precipitate, composed of microscopic needles. (Laurent.)

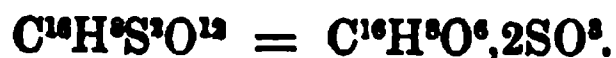
The ammonia-salt does not yield precipitates with the chlorides of cobalt and nickel; with acetate of copper, it forms a bluish-white precipitate; with mercurous nitrate, a white precipitate. Mixed warm with a solution of mercuric chloride, it deposits microscopic needles. (Laurent.)

*Anisate of Silver.* — Anisic acid forms, with oxide of silver, a colourless salt, but slightly soluble in cold water, crystallising from boiling water in fine needles. (Cahours.) — *Anisate of ammonia* gives, with a boiling solution of silver, a white precipitate, crystallising in needles (Laurent.) — The precipitate is composed of shining scales, greasy to the touch. (Hempel.)

				Cahours.	Laurent.	Hempel.
				<i>Dried in vacuum at 120°.</i>		
16 C .....	96	....	87.06	.....	37.04	.... 36.74
7 H .....	7	....	2.70	.....	2.37	.... 2.81
AgO .....	116	....	44.79	.....	44.71	.... 44.67
5 O .....	40	....	15.45	.....	15.88	.... 15.78
<hr/>						
C <sup>16</sup> H <sup>7</sup> AgO <sup>6</sup> .....	259	....	100.00	.....	100.00	.... 100.00

Anisic acid is readily soluble in alcohol and ether, especially with the aid of heat (Cahours, Laurent); the saturated alcoholic solution solidifies on cooling. (Persoz.)

According to Persoz, ombellic acid is but slightly soluble in cold ether; badianic acid easily; Hempel found no difference between the dissolved and the undissolved portion.

**Sulphanisic Acid.**

LOUIS ZERVAS. *Ann. Pharm.* 103, 339.

LIMPRICHT. *Briefliche Mittheilung.*

*Sulfanisinsäure, Anisschwefelsäure.*

**Preparation.** Anisic acid is heated with oil of vitriol to  $110^\circ$ , or mixed with so much fuming sulphuric acid that the mass remains syrupy, and heated for two hours in the water-bath, or till the solution obtained remains clear on being mixed with water; the liquid is then diluted with water, and carbonate of lead is added in excess; the solution is filtered while boiling, and the insoluble residue is repeatedly boiled with water, as long as needles of anisate of lead continue to form on the cooling of the filtrate. These, when decomposed by sulphuretted hydrogen, yield sulphanisic acid. (Zervas.) — Limpricht treats anisic acid with anhydrous sulphuric acid, and obtains the pure acid by decomposing the lead-salt with sulphuretted hydrogen.

**Properties.** When obtained by slow evaporation of the aqueous solution, it forms needles, permanent in air, which lose 6.9 p. c. water at  $100^\circ$  ( $2HO = 7.2$  p. c.) and are then not further altered at  $170^\circ$ . (Zervas.)

					Zervas.
2 S	.....	32	....	13.79	..... 14.12
$C^{16}H^8O^{12}$	.....	200	....	86.21	
<hr/>					
$C^{16}H^8S^2O^{12}$	.....	232	....	100.00	

The aqueous solution of sulphanisic acid may be boiled without undergoing decomposition.

The sulphanisates of ammonia, potash, and soda crystallise readily, the first in beautiful, long, slender needles.

*Sulphanisate of Baryta* is obtained by saturating the acid with carbonate of baryta. It forms beautiful crystals, which give off 4.7 p. c. water at  $170^\circ$ . (Zervas.) After drying over oil of vitriol, it gives off 16.9 p. c. (8 At.) water at  $180^\circ$ . (Limpricht.) Readily soluble in water, less soluble after repeated recrystallisation. (Zervas.)

Easily soluble in water; precipitated in needles from the aqueous solution, by alcohol. (Limpricht.)

					Zervas. at $100^\circ$ .
16 C	.....	96	....	24.92	
6 H	.....	6	....	1.56	
2 Ba	.....	137.2	....	35.62	..... 35.71
2 S	.....	32	....	8.31	
12 O	.....	96	....	24.92	
2 Aq	.....	18	....	4.67	..... 4.7
<hr/>					
$C^{16}H^6Ba^2S^2O^{12}, 2Aq$	....	385.2	....	100.00	

	At 180°.		Limpricht.	
$C^{16}H^6S^2O^{12}$ .....	230	....	62.64	
2 Ba .....	137.2	....	37.36	..... 37.1
<hr/>				
$C^{16}H^6Ba^2S^2O^{12}$ .....	367.2	....	100.00	

*Sulphanisate of Magnesia.* — Needles, readily soluble.

*Sulphanisate of Lead.* — *a. Acid.* — Nodular crystals easily soluble in cold and in hot water. After drying over oil of vitriol it loses 8.0 p. c. water (2 At.) at 180°. (Limpricht.)

	At 180°.		Limpricht.	
$C^{16}H^6S^2O^{12}$ .....	233	....	69.96	
Pb .....	104	....	30.04	..... 29.3
<hr/>				
$C^{16}H^6PbS^2O^{12}$ .....	337	....	100.00	

*b. Neutral.* — (Preparation p. 128). — Beautiful needles, which after drying at 100°, give off 3.81 p. c. water (calculation 3.95 p. c.) at 175°. (Zervas.) After drying over oil of vitriol, it gives off 14.8 p. c. water (8 At.) at 180°. (Limpricht.)

Scarcely soluble in cold water, readily in boiling water, but its solubility is diminished by repeated crystallisation. (Zervas.)

	Dried at 100°.		Zervas.	
16 C .....	96	....	21.05	..... 20.99
8 H .....	8	....	1.75	..... 1.79
2 Pb .....	208	....	45.60	..... 45.45
2 S .....	32	....	7.00	..... 7.05
14 O .....	112	....	24.60	..... 24.72
<hr/>				
$C^{16}H^6Pb^2S^2O^{12}, 2Aq$ .....	456	....	100.00	..... 100.00

*Sulphanisate of Silver.* — Obtained by treating the acid with carbonate of silver. Sparingly soluble in water, especially after recrystallising. (Zervas.) Nodular crystals, sparingly soluble in water. (Limpricht.)

### Anisate of Methyl.



CAHOURS. *N. Ann. Chim. Phys.* 14, 493; *J. pr. Chem.* 36, 429; further *N. Ann. Chim. Phys.* 23, 251; *J. pr. Chem.* 45, 147; *Pharm. Centr.* 1845, 900.

*Anissaures Methyloxyd, Anisate de Methylène, Anisformester.*

*Formation.* 1. From anisic acid and wood-spirit. — 2. Chloride of anisyl mixed with wood-spirit becomes heated and forms anisate of methyl, precipitable from the mixture by water.

*Preparation.* 2 parts of anhydrous wood-spirit are mixed with

1 part of crystallised anisic acid and 1 part oil of vitriol, and the deep carmine-red mixture is distilled. Wood-spirit passes over first, then anisate of methyl, as a heavy, quickly congealing oil, which is washed with a warm solution of soda, then with water, and crystallised two or three times from alcohol or ether.

*Properties.* White, shining, broad scales. Melts between  $46^\circ$  and  $47^\circ$  and solidifies into a white crystalline mass on cooling. Boils at a very high temperature and passes over undecomposed. Smells faintly of anise. Tastes hot and burning.

					Cahours.
18 C .....	108	...	65.06	.....	64.86
10 H .....	10	...	6.02	.....	6.06
6 O .....	48	...	28.92	.....	29.08
<hr/>					
$C^{18}H^{10}O^6$ .....	166	...	100.00	.....	100.00

Isomeric with ethylsalicylic acid.

*Decomposition.* 1. *Chlorine* and *bromine* act violently on anisate of methyl, eliminating large quantities of hydrochloric or hydrobromic acid, and yielding crystallisable products in which hydrogen is replaced by chlorine or bromine. — 2. Fuming *nitric acid* forms nitransate of methyl, with violent action. — 3. *Ammonia* seems to act with anisate of methyl in the same manner as with salicylate of ethyl (xii, 259). — 4. Concentrated *solution of potash* boiled with anisate of methyl yields wood-spirit and anisate of potash.

Anisate of methyl is insoluble in water, abundantly soluble in alcohol and ether, especially on the application of heat.

### Anisate of Ethyl.



CAHOURS. *N. Ann. Chim. Phys.* 2, 292; *J. pr. Chem.* 24, 351; *Compt. rend.* 19, 775; *N. Ann. Chim. Phys.* 14, 492; *J. pr. Chem.* 36, 427; further: *N. Ann. Chim. Phys.* 23, 351; *J. pr. Chem.* 45, 147; *Pharm. Centr.* 1845, 900.

*Anisic Ether, Anisvinester.*

*Formation.* 1. From anisic acid and alcohol. — 2. Chloride of anisyl mixed with strong alcohol becomes heated, and forms anisic ether precipitable by water.

*Preparation.* Absolute alcohol is nearly saturated with anisic acid at  $50^\circ$  —  $60^\circ$ ; hydrochloric acid gas is passed through the liquid as long as it continues to be absorbed; and the fuming liquid is distilled. From the liquid saturated with hydrochloric acid, water precipitates unaltered anisic acid. Chloride of ethyl passes over first, then alcohol, and lastly anisic ether, which, by washing with carbonate of soda and then with water, is freed from adhering hydrochloric acid, anisic acid and alcohol, and rectified over chloride of calcium. Cahours at first recommended a final rectification over excess of oxide of lead.

*Properties.* Colourless liquid, denser than water. Boils at 250° to 255°. Odour similar to that of anise-camphor; taste warm and spicy.

				Cahours.	
				formerly.	later.
20 C	.....	120	... 66·70	..... 66·76	... 66·56
12 H	.....	12	... 6·67	..... 6·28	... 6·76
6 O	.....	48	... 26·68	..... 26·96	... 26·68
<hr/>				<hr/>	
C <sup>20</sup> H <sup>12</sup> O <sup>6</sup>	.....	180	... 100·00	..... 100·00	... 100·00

*Decompositions.* 1. Anisic ether becomes slowly acid when exposed to the air. — 2. It is strongly heated by dropping *bromine* into it, evolving a large quantity of hydrobromic acid and solidifying in crystals of bromanisic ether. — 3. In dry *chlorine gas* it is converted into needles of chloroanisic ether. — 4. Anisic ether dissolves in fuming *nitric acid* with evolution of heat, forming nitranisic ether, precipitable by water. — 5. *Ammonia* does not dissolve the ether, but after long continued action forms crystalline anisamide. — 6. Boiled with a *solution of potash*, it is readily decomposed into alcohol and anisate of potash.

Anisic ether is insoluble in water, readily soluble in *alcohol* and *ether*.

### Hydrochlorate of Anisene C<sup>16</sup>H<sup>8</sup>O<sup>2</sup>,HCl ?

CANNIZARO u. BERTAGNINI.

The upper layer of liquid obtained by passing hydrochloric acid gas through anisalcohol (p. 120), yields, when washed with dilute solution of carbonate of potash and afterwards with water, a colourless oil, which has a fruity odour and burning taste, forms sal-ammoniac and anisalcohol when treated with alcoholic ammonia, and appears to be decomposed by aqueous solutions of the alkaline carbonates. It acts violently on anisalcohol, forming hydrochloric acid, anisic acid and a resin insoluble in alcohol and ether, soluble in chloroform.

### Thianisiol.



CAHOURS. *Compt. rend.* 25, 458.

*Hydruce de sulfanisyle.* (Gerhardt, *Traité* 3, 360.)

*Formation.* 1. By the action of sulphide of ammonium on alcoholic anisylous acid (p. 121). — 2. By the action of hydrosulphuric acid on anishydramide.

When hydrosulphuric acid is passed through alcoholic anishydramide to saturation, the liquid becomes turbid and deposits pulverulent thianisiol, which is obtained white by washing with alcohol.

*Oxybromine-nucleus*  $C^{16}H^7BrO^2$ .**Bromide of Anisyl.**

CAHOURS. *Compt. rend.* 19, 795; *N. Ann. Chim. Phys.* 14, 486; *J. pr. Chem.* 36, 422; abstr. *Ann. Pharm.* 56, 307.

*Bromure d'anisyle, Anisylbromür, Bromanisyl.*

**Formation and Preparation.** Anhydrous bromine is added drop by drop to anisylous acid (an excess of bromine must be avoided as it would yield a product richer in bromine). The mixture becomes strongly heated, gives off hydrobromic acid abundantly, and then solidifies. The product is at once washed with ether, which takes up an oil, and the residue is pressed between blotting paper and crystallised from ether. White, silky needles.

					Cahours.
16 C	.....	96	...	44.65	..... 44.47
7 H	.....	7	...	3.26	..... 3.49
Br	.....	80	...	37.21	..... 37.43
4 O	.....	32	...	14.88	..... 14.61
<hr/>					
$C^{16}H^7BrO^4$	.....	215	...	100.00	..... 100.00

It is perhaps bromanisylous acid. Gerhardt (*Traité* 3, 372).

Bromide of anisyl distils almost without decomposition. A strong boiling solution of potash converts it into bromide of potassium and anisate of potash.

**Bromanisic Acid.**

LAURENT. *Rev. scient.* 10, 16; *J. pr. Chem.* 27, 243.

CAHOURS. *N. Ann. Chim. Phys.* 14, 495; *J. pr. Chem.* 36, 430; abstr. *Ann. Pharm.* 56, 311.

*Acide bromodraconésique, bromodraconique, brodracasique, bromadracisique, bromoanisatiqué, bromoanisique.*

**Formation and Preparation.** When bromine is allowed to act on anisic acid, acid fumes are evolved and the liquid becomes hot. The residue is freed from excess of bromine by washing with a little cold alcohol, and dissolved in boiling alcohol; nearly all the bromanisic acid then separates on cooling. (Laurent.) Cahours removes the excess of bromine by water, and to remove a yellowish substance, presses between filtering paper the bromoanisic acid which has been crystallised from alcohol, and obtains the acid perfectly white by recrystallisation,

*Properties.* White, shining needles, which melt at  $204^{\circ}$  —  $205^{\circ}$ , volatilise without decomposition, and sublime in fine rectangular or rhombic, somewhat iridescent plates. (Laurent.)

					Laurent.		Cahours.
16 C	.....	96	...	41.55	.....	41.55	.... 41.71
7 H	.....	7	...	3.04	.....	2.96	.... 3.15
Br	.....	80	...	34.68	.....	34.46	.... 34.79
6 O	.....	48	...	20.78	.....	21.03	.... 20.35
<hr/>							
$C^{16}H^7BrO^6$	.....	231	...	100.00	.....	100.00	.... 100.00

Isomeric with methyl-bromosalicylic acid.

By distillation with excess of lime, or by dry distillation of the potash-salt, the acid is resolved into carbonic acid and bromanisol. (Cahours.)

Sparingly soluble in boiling water.

Bromanisic acid forms with ammonia and with the fixed alkalis, readily soluble, crystallisable-salts. (Cahours.) The ammonia-salt precipitates baryta- strontia- and lime-salts white, or if the solutions are somewhat dilute, yields needles; it does not precipitate magnesia-salts. It precipitates the lead-salts white. (Laurent.)

*Bromanisate of Silver.* — Bromanisate of ammonia forms with salts of silver a white precipitate, which, when dried at  $100^{\circ}$ , contains 32.14 p. c. of silver and is therefore  $C^{16}H^6BrAgO^6$  (calculation requires 31.97 p. c.). (Laurent.)

Bromanisic acid dissolves pretty readily in alcohol and ether, especially with the aid of heat.

### Bromanisate of Methyl.



CAHOURS. *N. Ann. Chim. Phys.* 14, 503; *J. pr. Chem.* 36, 436.

*Bromanisate de méthylène, Bromanisformester.*

*Formation and Preparation.* — 1. When bromine is poured drop by drop on anisate of methyl, the mass fuses from the heat produced, evolves much hydrobromic acid and becomes reddish-yellow. It is freed from bromine and hydrobromic acid by washing with water, and recrystallised several times from alcohol.

2. A solution of bromanisic acid in anhydrous wood-spirit is heated in the water-bath for a quarter of an hour with a little oil of vitriol, and the mixture is diluted with 3 or 4 times its volume of water, which causes an abundant precipitation of flakes. These are washed, first with ammoniacal, then with pure water, recrystallised from boiling strong alcohol, and pressed between paper.



*Properties.* Small, transparent prisms, melting at a gentle heat.

				Cahours.	
18 C	.....	108	....	44.08	..... 44.30
9 H	.....	9	....	3.67	..... 3.81
Br	.....	80	....	32.65	..... 32.63
6 O	.....	48	....	19.60	..... 19.26
<hr/>					
$C^{18}H^9BrO^6$	.....	245	....	100.00	..... 100.00

Decomposed into wood-spirit and bromanisate of potash on boiling with solution of potash.

Insoluble in water. Dissolves pretty readily in alcohol and wood-spirit, especially with the aid of heat, less readily in ether.

### Bromanisate of Ethyl.



CAHOURS. *N. Ann. Chim. Phys.* 14, 499; *J. pr. Chem.* 36, 336.

*Bromanisic ether, Bromanistvinester.*

*Preparation.* 1. When bromine is added drop by drop to anhydrous anisic ether, the liquid solidifies, with rise of temperature and evolution of hydrobromic acid. The mass, when freed by washing with water, from bromine and hydrobromic acid, pressed between paper and dissolved in boiling alcohol, crystallises on cooling. — 2. Hydrochloric acid gas is passed through a solution of bromanisic acid in absolute alcohol. The product obtained from the liquid, when washed, first with alkaline then with pure water, and several times crystallised from alcohol, exhibits the same properties as that obtained according to 1.

White, shining needles. Melts at a moderate heat, and volatilises when more strongly heated.

				Cahours.	
20 C	.....	120	....	46.33	..... 46.52
11 H	.....	11	....	4.24	..... 4.37
Br	.....	80	....	30.89	..... 30.94
6 O	.....	48	....	18.54	..... 18.17
<hr/>					
$C^{20}H^{11}BrO^6$	.....	259	....	100.00	..... 100.00

Boiled with a solution of potash, it splits up into alcohol and bromanisate of potash. Does not appear to be further changed by excess of bromine.

Dissolves readily in alcohol and ether, not in water.

### Oxychlorine-nucleus $C^{16}H^7ClO^3$ .

#### Chloride of Anisyl.



CAHOURS. (1848.) *N. Ann. Chim. Phys.* 23, 351; *J. pr. Chem.* 45, 147; extract *Ann. Pharm.* 70, 47.

*Formation and Preparation.* Pentachloride of phosphorus acts violently on anisic acid, eliminating a considerable quantity of hydrochloric

acid, and forming a mixture of chlorophosphoric acid and chloride of anisyl, from which the chlorophosphoric acid may be distilled off first, and then, chloride of anisyl collected in a fresh receiver between 250° and 270°. This product is washed with cold water, then with dilute solution of potash, and, after separation of the potash, rectified over chloride of calcium.

*Properties.* Colourless liquid of sp. gr. 1.26 at 15°. Has a penetrating odour. Boils at 262°.

				Cahours.	
16 C	.....	96	....	56.33	..... 56.05
7 H	.....	7	....	4.10	..... 4.30
Cl	.....	35.4	....	20.78	..... 20.98
4 O	.....	32	....	18.79	..... 18.67
<hr/>					
C <sup>16</sup> H <sup>7</sup> ClO <sup>4</sup>	.....	170.4	....	100.00	..... 100.00

*Decompositions.* 1. In contact with moist air, it rapidly forms hydrochloric and anisic acid. — 2. Becomes heated with strong wood-spirit or alcohol, whereupon water separates from the mixture the ether of anisic acid. — 3. With dry ammonia-gas it forms anisamide. — 4. With aniline it forms anisanilide.

Cahours had before obtained by the action of chlorine on anisylous acid, a crystalline product, to which he gave the formula C<sup>16</sup>H<sup>7</sup>ClO<sup>4</sup>, but which he did not examine more closely. (*Compt. rend.* 19, 795.)

### Chloranisic Acid.



LAURENT. (1842.) *Rev. scient.* 10, 15; *J. pr. Chem.* 27, 243.

CAHOURS. *N. Ann. Chim. Phys.* 14, 497; *J. pr. Chem.* 36, 432; *Pharm. Centr.* 1845, 901.

*Acide chlorodraconisque, chlorderacasique, chloranisatique, chloroanisique, Chloranissäure.*

*Formation.* By the action of chlorine on anisic acid.

*Preparation.* 1. Chlorine is passed through melted anisic acid, whereby hydrochloric acid is evolved, and the product is purified by crystallisation from alcohol. (Laurent.) — 2. When finely powdered anisic acid is introduced into a bottle filled with dry chlorine gas, the chlorine is rapidly absorbed, being replaced by hydrochloric acid gas. This is displaced by a current of dry air, and the solid product is washed with water and repeatedly crystallised from alcohol of 40°. (Baumé? Gm.) (Cahours.)

*Properties.* Colourless, slender, highly lustrous needles. Inodorous. Sublimes in rhombic needles with lateral edges of about 138° and 42°. (Laurent.) Melts at about 180° (Laurent); near 176°. (Cahours.) May be distilled without decomposition.

					Laurent.		Cahours.
16 C	.....	96	....	51.50	....	52.21	.... 51.47
7 H	.....	7	....	3.75	.....	3.68	.... 3.87
Cl	.....	35.4	....	19.00	.....	18.66	.... 18.97
6 O	.....	48	....	25.75	.....	25.45	.... 25.69
<hr/>							
$C^{16}H^7ClO^6$	.....	186.4	....	100.00	.....	100.00	.... 100.00

Isomeric with methyl-chlorosalicylic acid.

*Decompositions.* 1. The acid does not appear to be further changed by chlorine, even in sunshine. — 2. Heated with strong bases, it splits up into carbonic acid and chloranisol. The potash-salt yields by dry distillation an oil containing chlorine, probably chloranisol, and leaves a residue of carbonate of potash and charcoal. (Cahours.)

*Combinations.* Chloranisic acid is nearly insoluble in water. (Laurent.) It dissolves in warm sulphuric acid, partly crystallising in fine needles on cooling; water precipitates it completely from the solution.

With ammonia, potash, and soda, chloranisic acid forms soluble crystallisable salts. (Cahours.) The ammonia-salt forms crystalline precipitates with moderately diluted solutions of the chlorides of barium-strontium and calcium. It precipitates lead and silver-salts white. (Laurent.)

Chloranisic acid dissolves readily in alcohol and ether, especially on application of heat.

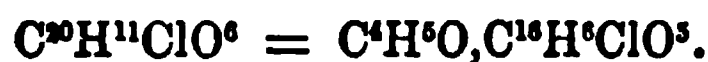
### Chloranisate of Methyl.



CAHOURS. (1845.) *N. Ann. Chim. Phys.* 14, 504; *J. pr. Chem.* 36, 434.

Anisate of methyl treated with dry chlorine, evolves hydrochloric acid and forms a crystallised compound, which when heated with potash is resolved into methylic alcohol and chloranisic acid.

### Chloranisate of Ethyl.



CAHOURS. *N. Ann. Chim. Phys.* 14, 500; *J. pr. Chem.* 36. 434.

*Preparation.* When anisic ether is poured into a bottle filled with chlorine, shining crystals soon make their appearance on the sides of the vessel, and are purified like bromanisate of ethyl (p. 134).

						Cahours.
20 C	.....	120	....	56.07	.....	55.93
11 H	.....	11	....	5.14	.....	5.07
Cl	.....	35.4	....	16.36	.....	16.17
6 O	.....	48	....	22.43	.....	22.83
<hr/>						
$C^{20}H^{11}ClO^6$	.....	214.4	....	100.00	.....	100.00

*Nitro-nucleus*  $C^{16}XH^9$ .

### Nitroxylol.



CAHOURS. *Compt. rend.* 30, 319.

CHURCH. *Phil. Mag. J.* 4, Ser. 9, 453; *J. pr. Chem.* 67, 44.

*Formation and Preparation.* Xylol forms, with fuming nitric acid, nitro- and binitro-xylol. (Cahours.)—2. Xylol, or the portion of light coal-tar oil boiling between  $124^\circ$  and  $130^\circ$  (p. 117), is dissolved in cold nitric acid of sp. gr. 1.5, and the product is precipitated by water, and freed from nitric acid by washing with water. (Church.)

*Properties.* Yellow oil heavier than water. Has a less pleasant odour than nitrobenzol. (Church.) It is transformed into xylidine by reducing agents. (Cahours, Church.) With fuming sulphuric acid it forms nitrosulphoxylic acid. (Church.)

### Nitrosulphoxylic Acid.



CHURCH. *Phil. Mag. J.* [4], 455; *J. pr. Chem.* 47, 45.

*Nitroxylschwefelsäure.*

Known only as a baryta-salt.

*Formation and Preparation of the Baryta-salt.*—Nitroxylol is dissolved in fuming oil of vitriol, and the solution, after being kept for an hour at a temperature of  $100^\circ$ , is left to itself for three days, then distilled with water, neutralised with carbonate of baryta, and filtered. The filtrate evaporated nearly to dryness, leaves nitrosulphoxylate of baryta in the form of a crystalline lemon-yellow powder.

				Church.
Ba .....	68.6	...	22.97	..... 22.5
$C^{16}NH^9S^2O^{10}$ .....	280	...	77.03	
<hr/>				
$C^{16}NH^9BaS^2O^{10}$ .....	298.6	...	100.00	

*Oxynitro-nucleus*  $C^{16}XH^7O^3$ .

### Nitranisic Acid.



CAHOURS. (1845.) *N. Ann. Chim. Phys.* 2, 297.

LAURENT. *Rev. scient.* 10, 13; *J. pr. Chem.* 27, 241; *Pharm. Centr.* 1846, 902.

*Acide nitroanisique, nitrodraconésique, nitranisatigue, Anissalpetersäure.*

*Formation.* By the action of boiling nitric acid on anise-camphor (Cahours) on oil of tarragon (Laurent), or on anisic acid,

**Preparation.** 1. Anise-camphor is boiled with nitric acid of 36° Bm. till the oil which first forms is perfectly dissolved in the boiling liquid; water is then added, which on cooling precipitates the nitranisic acid in yellow flakes. The product is washed with water till the washings have scarcely any acid taste, and then dissolved in ammonia; the ammonia-salt, after being several times recrystallised till scarcely a trace of yellow remains, is dissolved in water; and the nitranisic acid is precipitated by the addition of an acid: it is obtained pure by washing with distilled water. (Cahours.)—2. The mother-liquor of anisate of ammonia obtained in the preparation of anisic acid, which, besides *nitrodraconate d'ammoniaque*, contains already some nitranisate of ammonia, is precipitated by nitric acid; and the precipitate is washed with water, dried, and boiled with nitric acid for half an hour. On cooling, short four-sided prisms are deposited, which when washed with water and dissolved in boiling alcohol, are at once precipitated in fine needles on cooling. (Laurent.)

**Properties.** Colourless or pale-yellowish needles. It is deposited in small shining needles on the cooling of the boiling aqueous or weak alcoholic solution.—Melts at 175—180°, and sublimes at a higher temperature without decomposition. The angles of the lateral edges of the crystals obtained by sublimation, measure respectively about 114° and 66°; in those crystallised from nitric acid, to about 102°. (Laurent.) When carefully heated, it sublimes partly undecomposed, as a yellow powder, while another portion turns black and emits a suffocating odour. (Cahours.) Inodorous; tasteless. (Laurent.)

					Cahours.		Laurent.
16 C	.....	96	...	48.73	.....	48.81	.... 49.07
N	.....	14	...	7.11	.....	7.27	.... 7.37
7 H	.....	7	...	3.55	.....	3.10	.... 3.60
10 O	.....	80	...	40.61	.....	40.82	.... 39.96
<hr/>							
$C^{18}NH^7O^{10}$	.....	197	...	100.00	.....	100.00	.... 100.00

**Decompositions.** 1. In the distillation of 20—30 gr. of nitranisic acid, decomposition ensues, attended with emission of light, after a few grammes have passed over.—2. Nitranisic acid is not changed by nitric acid, chlorine or bromine. (Laurent.)—3. It is violently acted upon, when heated, by *pentachloride of phosphorus*, forming chlorophosphoric acid and a dark yellow liquid which behaves like nitrochloranisyl. (Cahours.)—4. With *sulphide of ammonium* it yields anisamic acid. (Zinin.)—5. By boiling with *sulphite of ammonia*, it is decomposed like nitronaphthalin. (Piria.)

**Combinations.** Nitranisic acid is very sparingly soluble in cold water, somewhat more in boiling water. (Cahours.)

With ammonia, potash and soda, nitranisic acid forms salts which are readily soluble in water. The *ammonia-salt* crystallises in beautiful needles, spherically grouped. (Laurent.) The baryta, strontia, lime and magnesia-salts of nitranisic acid are sparingly soluble. (Cahours.) The baryta and strontia-salts, obtained by precipitating nitranisate of ammonia with chloride of barium or strontium, form ramified needles; the lime-salt, a precipitate composed of small spherical granules; the magnesia-salt,

obtained from nitransate of baryta and sulphate of magnesia, forms radiated needles. From sulphate of manganese, nitransate of ammonia precipitates microscopic bundles of needles; from zinc-salts, a white precipitate composed of needles. It precipitates alumina-salts white; sesquichloride of iron yellow; cupric salts bluish-white; lead-salts white. The chlorides of cobalt and nickel and mercuric salts form but slight precipitates with nitransate of ammonia. (Laurent.)

*Nitransate of Silver.*—Nitransate of ammonia precipitates silver-salts white. (Laurent.)

<i>At 120° in vac.</i>				<i>Cahours.</i>	<i>Laurent.</i>
16 C	96	...	31.56	31.89	
N	14	...	4.61		
6 H	6	...	1.97	1.78	
Ag	108.1	...	35.55	35.52	35.67
10 O	80	...	26.31		
<hr/>					
$C^{16}NH^6AgO^{10}$	304.1	...	100.00		

Nitransic acid is insoluble in water. (Cahours.)

It is moderately soluble in hot alcohol; the solution solidifies on cooling. It dissolves in ether, especially on application of heat.

### Nitransate of Methyl.



CAHOURS. *N. Ann. Chim. Phys.* 14, 504; *J. pr. Chem.* 36, 435; *Pharm. Centr.* 1845, 903.

*Nitransate de méthylène, Nitranisformester.*

*Formation and Preparation.* 1. Nitransic acid is boiled with wood-spirit and oil of vitriol.—2. Anisate of methyl is dissolved in fuming nitric acid, and the product is precipitated by water, and crystallised several times from alcohol.

*Properties.* Broad, yellowish plates, very much resembling nitransate of ethyl. Melts near 100°, and volatilizes at a higher temperature.

				<i>Cahours.</i>
18 C	108	...	52.17	51.85
N	14	...	6.76	6.93
9 H	9	...	4.34	4.44
10 O	80	...	36.73	36.78
<hr/>				
$C^{18}NH^9O^{10}$	211	...	100.00	100.00

Heated with potash, it is resolved into wood-spirit and nitransate of potash.

Insoluble in water. Dissolves readily in hot wood-spirit and alcohol, the greater part being deposited in crystals on cooling.

**Nitranisate of Ethyl.**

CAHOURS. *N. Ann. Chim. Phys.* 14, 501.

MITSCHERLICH. *J. pr. Chem.* 22, 195; *Pharm. Centr.* 1845, 902.

*Nitranisic ether, Nitranisvinester.*

**Formation and Preparation.** 1. A solution of nitranisic acid in absolute alcohol is saturated at 60° to 70°, with hydrochloric acid gas. The liquid then becomes heated, turns yellow, evolves hydrochloric acid and chloride of ethyl, and when mixed with water, deposits thick yellowish flakes, which may be freed from uncombined nitranisic acid by washing with ammoniacal water; they are obtained pure, by washing with distilled water, drying, and repeated crystallisation from alcohol. — 2. When equal parts of anisic ether and fuming nitric acid are mixed, the ether dissolves in the acid with evolution of heat. The product is precipitated by water, well washed, and crystallised from alcohol. (Cahours.)

**Properties.** Beautiful, highly lustrous, broad plates. Crystallises well. (Mitscherlich.) Melts between 98° and 100°.

					Cahours.
20 C	.....	120	...	53.33	..... 53.12
N	.....	14	...	6.22	..... 6.14
11 H	.....	11	...	4.88	..... 5.15
10 O	.....	80	...	35.57	..... 35.59
<hr/>					
$C^{20}NH^{11}O^{10}$	.....	225	...	100.00	..... 100.00

**Decompositions.** It is rapidly decomposed by alcoholic potash, into alcohol and nitranisic acid. Not altered by bromine.

Nitranisate of ethyl is insoluble in water. It dissolves in oil of vitriol, especially on application of heat; on cooling, part of the ether crystallises out, and the whole is precipitated by water.

Dissolves abundantly in hot alcohol and crystallises from it almost completely. (Cahours.)

**Aniso-nitranisic Acid.**

LAURENT. *Rev. scient.* 16, 11; *J. pr. Chem.* 27, 239. Also *Compt. rend.* 20, 366.

BERZELIUS. *Jahresb.* 23, 420.

*Acide nitrodraconasique.*

**Formation and Preparation.** The mother-liquor, from which anisate of ammonia has separated (p. 224), contains (besides anisic acid)

ammonia-salts of aniso-nitranisic acid and nitranisic acid. It is evaporated nearly to a syrup, and boiled in a flask with alcohol, which dissolves it entirely and deposits crystals on cooling. The mother-liquor yields more crystals by repeated evaporation. All these crystalline deposits are dissolved in boiling alcohol, and the solution is slowly cooled, whereby crystals of aniso-nitranisate of ammonia are obtained. The crystals should deposit in radiated hemispheres, which form first on the surface of the fluid, gradually increase, and then fall to the bottom; should single needles form, the liquid must be poured off at once.

The ammonia-salt is purified by two or three crystallisations from alcohol, dissolved in boiling water with addition of ammonia, and nitric acid added. A white precipitate immediately forms, which must be collected on a filter, washed and dried.

*Properties.* May be obtained crystallised in flat needles by the cooling of a boiling alcoholic solution. Yellowish-white. Has a scarcely perceptible taste. Melts at  $185^{\circ}$ , and solidifies to a radiated mass on cooling. May be sublimed without decomposition in rhombic needles, the angles of whose obtuse lateral edges are about  $101^{\circ}$ .

					Laurent.
32 C	.....	192	...	55.00	..... 54.95
N	.....	14	...	4.01	..... 4.50
15 H	.....	15	...	4.29	..... 4.26
16 O	.....	128	...	36.70	..... 36.29
<hr/>					
$C^{32}NH^{15}O^{16}$	.....	349	...	100.00	..... 100.00

According to Gerhardt, this substance is probably a mixture of anisic acid and nitranisic acid in definite proportions. — Laurent did not however succeed in decomposing aniso-nitranisic acid by repeated crystallisation. (*Compt. rend.* 20, 336.)

*Decompositions.* 1. It is transformed by bromine into bromaniso-nitranisic acid, by chlorine into chloraniso-nitranisic acid. — 2. With nitric acid it yields nitranisic acid.

*Combinations.* The acid is nearly insoluble in water. It forms with ammonia a sparingly soluble salt, crystallising in radiated spheres; the solution behaves towards other saline solutions like nitranisate of ammonia.

Aniso-nitranisic acid is readily soluble in alcohol and ether.

### Bromaniso-nitranisic Acid.



LAURENT. *Rev. scient.* 10, 17; *J. pr. Chem.* 27, 245; *Compt. rend.* 20, 366.

*Acide nitrobromodraconésique.*

Bromine is poured upon aniso-nitranisic acid, and the decomposition, which commences at once, is finally promoted by heat. The residue is



washed with cold alcohol, and then dissolved in hot alcohol, from which the acid crystallises in laminar needles on cooling.

Melts at  $175^\circ$  —  $180^\circ$ , and then sublimes in rhombic or six-sided plates.

					Laurent.
32 C	.....	192	...	44.86	..... 44.41
Br	.....	80	...	18.69	
N	.....	14	...	3.27	..... 3.51
14 H	.....	14	...	3.27	..... 3.37
16 O	.....	128	...	29.91	
<hr/>					
$C^{32}BrNH^{14}O^{16}$	.....	428	...	100.00	

The acid does not dissolve in water. It forms an ammonia-salt, the solution of which behaves towards the solutions of other salts like nitranisate of ammonia.

It is soluble in alcohol and ether.

### Chloraniso-nitranisic Acid.



LAURENT. *Rev. scient.* 10, 18; *J. pr. Chem.* 27, 247.

#### *Acide nitrochlorodraconésique.*

Chlorine gas is passed through melted aniso-nitranisic acid, the mass is dissolved in boiling alcohol, and the solution left to crystallise.

Crystallises from alcohol and ether in small colourless needles. Melts at  $170^\circ$ , then sublimes in small acicular, oblique prisms.

					Laurent.
32 C	.....	192	...	50.08	..... 50.18
Cl	.....	35.4	...	9.23	
N	.....	14	...	3.65	
14 H	.....	14	...	3.65	..... 3.76
16 O	.....	128	...	33.39	
<hr/>					
$C^{32}ClNH^{14}O^{16}$	.....	383.4	...	100.00	

Insoluble in water. The ammonia-salt forms crystalline precipitates with the somewhat dilute solutions of the chlorides of barium, strontium and calcium. It precipitates chloride of manganese, white; chloride of cobalt, pale pink; chloride of copper, bluish-white; the nitrates of lead, mercury and silver, white.

The acid dissolves in hot alcohol and ether.

### Chloride of Nitranisyl.



CAHOURS. (1848.) *N. Ann. Chim. Phys.* 23, 354; *J. pr. Chem.* 45, 150; *Pharm. Centr.* 1848, 600.

Nitranisic acid, when warm, is violently acted upon by pentachloride of phosphorus; and on distilling the residue, chlorophosphoric acid passes

over first, then, at a high temperature, a dark-yellow liquid, which in contact with moist air is decomposed into hydrochloric acid and nitranisic acid, and yields with alcohol nitranisic ether.

*Oxynitro-nucleus*  $C^{16}X^3H^5O^3$ .

**Ternitranisic Acid.**



CAHOURS. *Compt. rend.* 24, 557.

Anisic acid is treated in the cold with a mixture of fuming nitric acid and fuming oil of vitriol, and the whole diluted with 8 or 10 times its volume of water.

Forms very beautiful salts with the alkalis, especially with ammonia and potash.

*Oxyamidogen-nucleus*  $C^{16}AdH^7O^3$ .

**Anisamide.**



CAHOURS. (1848.) *N. Ann. Chim. Phys.* 23, 353; *J. pr. Chem.* 45, 149; *Pharm. Centr.* 1848, 599. .

*Preparation.* 1. Chloride of anisyl (p. 134) is treated with dry ammonia-gas, and the resulting mass is dissolved in alcohol and set aside for spontaneous evaporation. — 2. Ammonia is made to act on anisic ether.

Beautiful prisms.

					CAHOURS.
16 C	.....	96	...	63.58	..... 63.43
N	.....	14	...	9.27	..... 9.48
9 H	.....	9	...	5.96	..... 6.01
4 O	.....	32	...	21.19	..... 21.08
<hr/>					
$C^{16}NH^9O^4$	.....	151	...	100.00	..... 100.00

Isomeric with benzamate (amidobenzoate) of methyl (xii, 146).

**Amidanisic Acid.**



ZININ. (1855.) *Petersb. Acad. Bull.* 12, 236; *Ann. Pharm.* 92, 327 ; *Pharm. Centr.* 1854, 354.

CAHOURS. *Compt. rend.* 44, 568; *Pharm. Centr.* 1857, 465.

*Anisamic acid.*

*Formation and Preparation.* 8 parts of alcohol of 90 p. c. are saturated with gaseous ammonia, 1 part of nitranisic acid is added, and

hydrosulphuric acid passed through the liquid. After 12 hours, the whole is dissolved to a yellow fluid, which, when heated to boiling, gives off sulphide of ammonium and deposits sulphur. The liquid is filtered, mixed with water and evaporated, to expel the alcohol and the hydrosulphuric acid. The solution of amidanisable of ammonia thus obtained yields on addition of acetic acid needles of amidanisable acid, which are obtained colourless by treating the aqueous solution with animal charcoal. (Zinin.)

*Properties.* Crystallises from the aqueous solution in thin, four-sided, brilliantly shining prisms several inches long; from alcohol in thicker acicular prisms. Does not change at  $140^\circ$ ; melts at  $180^\circ$  to a yellow liquid, which on cooling solidifies in a crystalline mass. The aqueous solution has an acid reaction and a disagreeable sweetish-acid taste. (Zinin.)

At $120^\circ$ .				Zinin.
16 C	.....	96	... 57.48	..... 57.62
N	.....	14	... 8.38	..... 8.71
9 H	.....	9	... 5.39	..... 5.53
6 O	.....	48	... 28.75	..... 28.14
<hr/>				
$C^{16}NH^7O^6$	.....	167	... 100.00	..... 100.00

Stands in the same relation to nitranisable acid as amidobenzoic acid to nitrobenzoic acid.

*Decompositions.* 1. When carefully heated on platinum-foil, it volatilises, emitting white vapours which have a faint odour. — 2. When heated above  $180^\circ$ , it acquires a brown colour, and yields by distillation a colourless, readily solidifying liquid, which is not amidanisable acid, while nothing but a little charcoal remains behind. — 3. Dissolves in hot diluted nitric acid, without at first undergoing any change; by long continued boiling, the solution acquires a red colour, and on cooling deposits a mixture of brown flakes and a white powder. (Zinin.)

*Combinations.* Amidanisable acid dissolves in 800 parts of boiling water, and is still less soluble in cold water. Crystallises unchanged from moderately strong hydrochloric acid. (Zinin.)

With hydrochloric acid it forms a readily crystallisable compound. (Cahours.)

*Amidanisable of Ammonia.* — Amidanisable acid forms with ammonia a readily soluble salt, which, when the concentrated solution is left to evaporate, crystallises with difficulty in square plates; the solution when much concentrated by boiling, deposits a portion of the amidanisable acid as it cools.

The aqueous solution of amidanisable acid does not precipitate lime- or baryta-water.

Amidanisable of ammonia forms with cadmium- and lead-salts, white pulverulent precipitates. — Aqueous amidanisable acid precipitates from ammonio-oxide of copper (oxide of cuprammonium) light-blue flakes, which on boiling, become cinnamon-coloured and pulverulent.

*Amidanisable of Silver.* — Amidanisable of ammonia forms with salts of silver a white, curdy precipitate, readily soluble in ammonia and in

acids, insoluble in water; dried at  $120^{\circ}$  it contains 39.25 p. c. of silver (the formula  $C^{16}NH^3AgO^6$  requires 39.43 p. c.). It does not change in the dark at  $120^{\circ}$ , but turns black when boiled with the liquid. Aqueous amidanisisic acid does not precipitate silver-salts. (Zinin.)

*Chloroplatinate of Amidanisisic Acid* —  $C^{16}NH^3O^6, HCl, PtCl^2$  — When amidanisisic acid is treated with a slight excess of hydrochloric acid, the residue dissolved in boiling alcohol and an excess of bichloride of platinum added, the compound crystallises on evaporation in brown-red prisms. (Cahours.)

Amidanisisic acid dissolves readily in alcohol, less readily in ether. It crystallises unchanged from boiling acetic acid.

*Conjugated compounds, containing a nucleus derived from  $C^{16}AdH^1O^3$ .*

### Anisanilide.



CAHOURS. (1848.) *N. Ann. Chim. Phys.* 23, 353; *J. pr. Chem.* 45, 149; *Pharm. Centr.* 1848, 600.

*Thianylanisamide, Nitride of anisyl, phenyl and hydrogen.*

Chloride of anisyl is treated with aniline, and the mass, whose formation is attended with evolution of heat, is purified by repeated crystallisation from alcohol. Delicate needles which sublime at a low temperature.

					Cahours.
28 C	.....	168	...	74.01	..... 73.94
N	.....	14	...	6.17	..... 6.44
13 H	.....	13	...	5.72	..... 5.85
4 O	.....	32	...	14.10	..... 13.77
<hr/>					
$C^{28}NH^{12}O^4$	.....	227	...	100.00	..... 100.00

### Anishydramide.



CAHOURS. (1845.) *N. Ann. Chim. Phys.* 14, 487; *J. pr. Chem.* 36, 424; also *Ann. Pharm.* 56, 309; *Compt. rend.* 25, 458.

BERTAGNINI. *Ann. Pharm.* 88, 128.

*Hydrure d'azoisyle.* (Gerhardt.)

*Formation.* By the action of ammonia on anisylous acid (p. 121).

*Preparation.* When 1 vol. of anisylous acid is left to stand in a closed vessel with 4 — 5 vol. of aqueous ammonia, the mixture gradually

deposits beneath the oily liquid; shining crystals, which increase, till in course of a month, the whole is transformed into a crystalline mass, which is freed from some admixed oil by pressing between blotting paper.

*Properties.* Colourless, hard prisms. May be pulverised. Has a faint odour, which is difficult to remove. (Cahours.) Melts at about  $120^\circ$  to a yellowish-brown liquid. (Bertagnini.)

				Cahours.	
48 C	.....	368	....	74.23	..... 74.23
2 N	.....	28	....	7.21	..... 7.31
24 H	.....	24	....	6.18	..... 6.14
6 O	.....	48	....	12.38	..... 12.32
<hr/>					
$C^{48}N^2H^{24}O^6$	.....	468	....	100.00	..... 100.00

Isomeric with anisine; stands in the same relation to salicylous acid as hydrobenzamide to oil of bitter almonds.

*Decompositions.* 1. Transformed into anisine when kept for two hours at  $165^\circ$  —  $170^\circ$ . (Bertagnini.) — 2. When dissolved in alcohol it yields thianisiol with sulphide of ammonium. (Cahours.)

*Combinations.* Insoluble in water. Dissolves in gently heated hydrochloric acid, and crystallises on cooling. Dissolves in hot alcohol and ether, crystallising from the solutions on cooling.

### Anisine.



BERTAGNINI. *Ann. Pharm.* 88, 128.

*Formation and Preparation.* Anishydramide is heated for two hours in the oil-bath to  $165^\circ$  —  $170^\circ$ ; and the fused product is dissolved in boiling alcohol and mixed with hydrochloric acid. The liquid, on cooling, solidifies to a crystalline mass, which, when freed of the mother-liquor and mixed with potash or ammonia, yields anisine.

*Properties.* Transparent prisms. The solutions have a strong alkaline reaction and a bitter taste.

*Combinations.* Nearly insoluble in boiling water.  
The anisine-salts are crystallisable.

*Hydrochlorate of Anisine.* —  $C^{48}N^2H^{24}O^6, HCl$ . — White shining needles. Dried at ordinary temperatures, it contains  $2\frac{1}{2}$  atoms of water, which are expelled at  $100^\circ$ . Sparingly soluble in water, readily soluble in alcohol.

*Chloroplatinate of Anisine.* —  $C^{48}N^2H^{24}O^6, HCl + PtCl^2 ?$  — Shining, pale orange scales; sparingly soluble in alcohol.

Anisine dissolves in alcohol, but sparingly in ether.

*Amo-nucleus*  $C^{16}NH^6$ .

### Xylidine.



CHURCH, *Phil. Mag. J.* [4] 9, 453.

*Formation and Preparation.* Nitroxylol is transformed into xylidine by reducing agents. (Cahours.) For its purification, the oxalate of xylidine is repeatedly crystallised, and then decomposed by distillation with lime. When the nitroxylol has been prepared from crude xylol, the xylidine is contaminated with cumidine and toluidine. In this case, the distillate is dissolved in hydrochloric acid; a sufficient quantity of bichloride of platinum is added; the precipitate which may form is dissolved in a little water; and the whole is left to evaporate over sulphuric acid. The crystals which form first are chloroplatinate of cumidine, and afterwards the double salt of xylidine forms in short yellow needles which, when distilled with soda, yield the xylidine nearly colourless. (Church.)

*Properties.* Nearly colourless oil, boiling at  $218^\circ - 214^\circ$ , and having a faint alkaline reaction.

Isomeric with ethylaniline, bimethylaniline, ethylopicoline and colidine.

*Decompositions.* Xylidine rapidly absorbs oxygen from the air, acquiring a red colour, and is gradually transformed into resin.

*Sulphate of Xylidine.* — Crystallises from water in long, colourless needles.

Church.				
$C^{16}NH^{12}O$ .....	180	...	76.48	
$SO^3$ .....	40	...	23.52	..... 23.41
<hr/>				
$C^{16}NH^{12}, HO, SO^3$ .....	170	...	100.00	

Sparingly soluble in cold water; the solution has an acid reaction.

*Chloroplatinate of Xylidine.* — (Preparation, see above.) — Short, yellow needles, grouped in stars, or truncated orange prisms.

Church.				
Pt .....	98.7	...	30.19	..... 30.27
$C^{16}NH^{12}Cl^3$ .....	228.2	...	69.81	
<hr/>				
$C^{16}NH^{11}, HCl, PtCl^3$ ....	826.9	...	100.00	

## Collidine.



TH. ANDERSON. (1855.) *N. Phil. Mag. J.* 9, 145, 214; *Pharm. Centr.* 1855, 259; *Chem. soc.* 7, 97; *Ann. Pharm.* 94, 360; *N. Ann. Chim. Phys.* 44, 501.

GREVILLE WILLIAMS. *New. Edin. Phil. J.* 2, 324; *Chem. Gaz.* 1855, 308; *J. pr. Chem.* 66, 338; *N. Ann. Chim. Phys.* 45, 490.

*Formation.* In the dry distillation of animal substances and of coal.

*Preparation.* 1. The portion boiling above  $170^{\circ}$  of the mixture of volatile bases obtained from bone-oil (x, 150; xii, 337), is mixed with a considerable quantity of strong nitric acid, which acts very violently upon it, thereby acquiring a deep red colour, and on boiling evolves nitrous acid fumes, and an odour of bitter almonds. The part boiling at  $182^{\circ}$  must be well cooled while being mixed with the nitric acid, to prevent explosion. The acid solution mixed with water, becomes turbid from the separation of a reddish-yellow oil, which seems to be impure nitrobenzol; the acid solution is filtered through moist paper, and the filtrate is boiled for some time to expel the last traces of the neutral oils, then saturated with potash and distilled. The oil which passes over with the water is repeatedly rectified, and the portion boiling between  $178^{\circ}$  and  $180^{\circ}$  is collected. The part of the mixture of bases boiling above  $170^{\circ}$  contains a considerable quantity of aniline, which cannot be removed, either by repeated rectification or by recrystallisation of the oxalate; by the action of nitric acid it is destroyed, whilst the alkalis homologous with collidine remain undecomposed. — The part boiling between  $172^{\circ}$ — $180^{\circ}$ , when treated in this manner, yields by distillation with potash, an oil which begins to boil at  $160^{\circ}$ , and is composed for the most part of lutidine; only the portion boiling above  $180^{\circ}$  yields an oil, which distils over for the most part at  $179^{\circ}$ , and when rectified yields pure collidine. (Anderson.) — 2. When the mixture of chinoline with other bases, which is obtained by the distillation of cinchonine with potash, is subjected to oft-repeated fractional distillation, the portion boiling between  $177^{\circ}$  and  $182^{\circ}$  yields, with solution of platinum, chloroplatinate of collidine. This salt may also be obtained from the fraction boiling between  $182^{\circ}$  and  $187^{\circ}$  if another base mixed with it has previously been destroyed by means of nitric acid. (Gr. Williams.)

3. Gr. Williams mixes the naphtha obtained by the distillation of the bituminous shale of Dorsetshire with sulphuric acid; boils with water until all the tar is converted into resin, and all the pyrrol is removed; concentrates the liquid; neutralises with lime or potash and distils; supersaturates the distillate with hydrochloric acid; removes the non-basic oil; then supersaturates the acid liquid with lime or potash, and distils. The distillate is freed from ammonia by washing with strong potash, then dried by solid hydrate of potash, and fractionally distilled until liquids of constant boiling points are obtained. The small portion which passes over between  $132^{\circ}$  and  $138^{\circ}$  is lutidine mixed with a little picoline (the mother-liquor of the chloroplatinate of lutidine yields the double salt of picoline); the portion obtained between  $149^{\circ}$  and  $155^{\circ}$ , and between  $177^{\circ}$  and  $182^{\circ}$  is pure lutidine; and that which passes over

between  $227^{\circ}$  and  $258^{\circ}$ , is collidine. The small quantity which distils over above  $260^{\circ}$  contains parvoline,  $C^{18}NH^{13}$ . — 4. The mixture of volatile alkalis obtained from coal-oil (xii, 337) is treated, as in 1, with nitric acid, and subjected to oft-repeated fractional distillation; the part passing over between  $150^{\circ}$  and  $155^{\circ}$  is lutidine, and after it a small quantity of collidine passes over. (Greville Williams.)

*Properties.* Colourless liquid, having a strongly aromatic, not disagreeable odour. Sp. gr. 0.921. Boiling point  $179^{\circ}$ . Forms white fumes with a glass rod moistened with hydrochloric acid. (Anderson.)

				Anderson.		Greville Williams.		
16 C	.....	96	... 79.33	.....	79.03	...	79.34	... 79.43
N	.....	14	... 11.58	.....	11.56	...	11.55	... 11.76
11 H	.....	11	... 9.09					
<hr/>								
$C^{16}NH^{11}$	.....	121	... 100.00					

Isomeric with bimethylaniline, ethylaniline, ethylopicoline, and xylidine.

The collidine examined by Anderson had been prepared from bone-oil; that examined by Gr. Williams from shale-oil.

Insoluble in water. It dissolves a small quantity of water, which it again gives up to hydrate of potash. Dissolves readily in acids, but does not neutralise them. It does not precipitate the salts of baryta, magnesia, lime, manganese, or nickel. It precipitates alumina, sesquioxide of chromium, oxide of zinc, sesquioxide of iron, and mercurous oxide from their solutions; it forms a precipitate with nitrate of lead, but not with the neutral acetate. (Anderson.)

With corrosive sublimate it forms a double salt, which precipitates in curdy flakes, and crystallises from hot water in needles. (Anderson.)

*Chloroplatinate of collidine* forms orange-yellow flakes.

				Anderson.		Gr. Williams.		
						a.	b.	c.
16 C	.....	96	... 29.33	.....	28.88	...	29.30	... 29.40
N	.....	14	... 4.31					
12 H	.....	12	... 3.66	.....	3.60	...	3.55	... 3.83
Pt	.....	98.7	... 30.16	.....	30.18	...	29.99	... 30.08
3 Cl	.....	106.5	... 32.54					... 30.07
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$C^{16}NH^{11}, HCl + PtCl^2$	...	327.2	... 100.00					

The salt analysed by Anderson was prepared from bone-oil; that analysed by Gr. Williams, (a) from cinchonine; b from coal-tar-oil; c from shale-oil.

Collidine dissolves readily in *alcohol*, in *ether*, and in *oils* both fixed and volatile. (Anderson.)

### Ethylcollidine.



ANDERSON. *N. N. Phil. Mag. J.* 9, 221; *Ann. Pharm.* 94, 365.

When iodide of ethyl is heated with collidine in the water-bath, an oily liquid separates, which, when freed from excess of iodide of ethyl, is



not obtained in the crystalline form, either by cooling or by addition of ether to its solution in a minimum quantity of absolute alcohol.

*Chloroplatinate of Ethylcollidine.* — The oily iodide of ethylcollidine is decomposed by nitrate of silver; the excess of silver is precipitated from the filtrate by hydrochloric acid; and the filtrate is mixed with a concentrated solution of bichloride of platinum. A finely divided, crystalline, sparingly soluble precipitate is thereby obtained.

Anderson.

20 C	.....	120	...	34.06	
16 H	.....	16	...	4.50	
N	.....	14	...	3.68	
3 Cl	.....	106.4	...	29.98	
Pt	.....	98.7	...	27.78	..... 27.65
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$C^{20}NH^{16}, HCl, PtCl^2$	.....	355.1	...	100.00	

*Primary-nucleus*  $C^{16}H^{13}$ .

*Oxygen-nucleus*  $C^{16}H^{10}O^3$ .

**Beta-orcin.**



J. STENHOUSE. (1848.) *Ann. Pharm.* 68, 104; *Phil. Mag. J.* 33, 300; *J. pr. Chem.* 45, 181.

*Formation and Preparation.* 1. When dried crude usnic acid is submitted to dry distillation, a portion of the beta-orcin sublimes in large yellow crystals, but the greater part passes over in the resinous distillate, and may be extracted from the resin by repeated boiling with water. The decoction is evaporated to the consistence of syrup and allowed to stand in an open vessel. After two or three days, brown crystals are formed, which are freed from resinous and colouring matters by pressing between folds of paper, then by treating the aqueous solution with animal charcoal and repeatedly crystallising. The product is finally obtained pure by crystallising it from weak alcohol, care being taken to remove quickly the mother-liquors, which turn red on exposure to the air.

2. Usnic acid is boiled with baryta or lime; carbonic acid passed through the solution; the filtered liquid evaporated to dryness; and the residue extracted with ether, which deposits yellowish crystals on evaporation. The crystals are purified as in 1. This process is not so productive as the former.

*Properties.* Beta-orcin crystallises from alcohol in large, well-defined, brilliant prisms, belonging to the quadratic system; they are shorter than those obtained from water.  $\infty P. P. \frac{1}{2} P. oP. \infty P \infty$ . (Miller.)

Tastes slightly sweet. Neutral. Does not melt at  $109^\circ$ . When heated, it sublimes completely in suffocating vapours. The crystals,

dried in the air, do not lose weight in *vacuo* over sulphuric acid, but on heating them to 100°, water evaporates, together with a large quantity of beta-orcin, so that the loss amounts to 30 per cent. and more,

<i>Dried in vacuo over sulphuric acid.</i>				<i>Stenhouse.</i>			
16 C	.....	96	....	69.56	.....	68.70	.... 69.20
10 H	.....	10	....	7.24	.....	7.22	.... 7.50
4 O	.....	32	....	23.20	.....	24.08	.... 23.20
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C <sup>16</sup> H <sup>10</sup> O <sup>4</sup>	.....	188	....	100.00	.....	100.00	.... 100.00

Stenhouse gave the empirical formula C<sup>68</sup>H<sup>24</sup>O<sup>10</sup>, which requires 68.68 per cent. C, and 7.22 H. Gerhardt gave the above. According to a previous conjecture of Strecker, it is C<sup>64</sup>H<sup>18</sup>O<sup>6</sup>.3HO (calculated 68.7 C and 7.1 H); by which its formation from usnic acid, supposing the formula of the latter to be C<sup>68</sup>H<sup>18</sup>O<sup>14</sup>, is explained as follows:



It is homologous with orcin. (Gerhardt, *Compt. chim.* 1849, 127.)

**Decompositions.** 1. Beta-orcin is readily inflammable, and burns with a very smoky flame. — 2. When treated with ammonia, it assumes a magnificent blood-red colour in a few minutes, more rapidly than orcin; it becomes darker on standing, but not reddish-brown like orcin. — 3. With carbonate of potash, or caustic potash, it forms a purple-red colouring matter, probably the same amorphous red body that Knop observed in the preparation of usnate of potash (*Ann. Pharm.* 49, 107). — 4. When treated with a solution of chloride of lime, it turns blood-red, but not violet.

**Combinations.** Beta-orcin is much less soluble in cold water than orcin; it is readily soluble in boiling water.

Its alcoholic solution does not precipitate the salts of baryta, lead, iron, copper, or nitrate of silver, not even on the addition of ammonia. Subacetate of lead produces a precipitate which is soluble in excess, very unstable, and quickly turns deep red on exposure to the air.

Beta-orcin dissolves readily in alcohol and in ether.

*Azo-nucleus* C<sup>16</sup>NH<sup>11</sup>.

### Sparteine.

J. STENHOUSE. (1851.) *Ann. Pharm.* 78, 15; *Pharm. Centr.* 1851, 439.

**Source.** From *Spartium scoparium*.

**Preparation.** Finely divided *Spartium scoparium* is exhausted by six or eight hours boiling with water, and the extract is reduced to one-tenth of its bulk. After 24 hours, the solution deposits a leaf-green gelatinous mass, containing scoparin, which is strained off and washed with a little water. On dissolving the residue in boiling water, slightly acidulating with hydrochloric acid, and filtering, the solution again solidifies, when

cold, into a gelatinous mass, which is strained, and pressed, and washed with a little water. The acid mother-liquor, reduced by evaporation and distilled with an excess of carbonate of soda, yields a strongly bitter distillate, which, when saturated with common salt and rectified, gives off first ammonia and then sparteine in small quantities, as a heavy colourless oil. By repeatedly pouring back the aqueous distillate, more sparteine may be obtained. The product is purified by drying it with chloride of calcium, and distilling it alone in a stream of carbonic acid; or it is dried in vacuo over sulphuric acid as long as it continues to lose weight. The smaller plants, grown in sunny places, yield the largest product.

*Properties.* Colourless, perfectly transparent, viscid oil. Heavier than water. Boils at  $288^{\circ}$ . Has a strong alkaline reaction, and a slight odour like that of aniline; after rectification it possesses a different and disagreeable odour. It has a very bitter taste, and highly narcotic properties, but is inferior in that respect to conine and nicotine. A drop dissolved in acetic acid, and administered to a rabbit or a small dog, causes excitement, followed by a state of stupor, which lasts for 5 or 6 hours. 4 grains killed a large rabbit, first producing excitement and then sleep, not accompanied by strong convulsions.

I.				II.				Stenhouse.	
								a.	b.
15 C	90	76.91	.....	16 C	96	78.05	.....	76.68	76.70
N	14	11.99	.....	N	14	11.38	.....		
13 H	13	11.10	.....	13 H	13	10.57	.....	11.01	11.17
$C^{16}NH^{12}$ .... 117 .... 100.00				$C^{16}NH^{12}$ .... 123 .... 100.00					

*a* was dried over chloride of calcium and rectified, *b* in vacuo over sulphuric acid. The first formula is given by Stenhouse; the second by Gerhardt (*Traité*, 4, 236), where, however, the percentage composition is wrongly calculated.

*Decompositions.* 1. Sparteine, exposed to the air for a few days, turns brown. — 2. It turns yellowish during distillation. — 3. When treated with bromine, it becomes heated, and is converted into a brown resin. — 4. When boiled with an excess of hydrochloric acid, it is decomposed and yields a solution which smells of mice. — 5. It is slowly decomposed by boiling with fuming nitric acid. Water added to the solution after the nitric acid has evaporated off, precipitates light flakes. The liquid filtered from the flakes yields chloropicrin when treated with chloride of lime, and a volatile base when saturated with potash and distilled. — 6. Sparteine does not yield aniline by distillation with potash.

*Combinations.* Sparteine is slightly soluble in water, but itself takes up a little water and becomes turbid.

Sparteine completely saturates acids. The chloride and nitrate cannot be obtained crystallised in vacuo.

A solution of sparteine precipitates a green compound from neutral chloride of copper. It precipitates neutral and basic acetate of lead.

*Chloromercurate of Sparteine.* — A solution of sparteine in hydrochloric acid forms, with chloride of mercury, a white crystalline precipitate,

which must be filtered, washed, and recrystallised from warm dilute hydrochloric acid. It forms very brilliant right square prisms. ( $\infty \check{P} \infty$ .  $\infty \bar{P} \infty$ .  $\infty \bar{P} 2$ .  $P$ .  $\check{P} \infty$ .) (Miller.) It does not give off water when heated to  $100^\circ$  in vacuo. It is scarcely soluble in water, but dissolves readily on the addition of hydrochloric acid. Almost insoluble in alcohol.

I.				
15 C	.....	90	....	31.14
N	.....	14	....	4.84
14 H	.....	14	....	4.87
Hg	.....	100.2	....	34.62
2 Cl	.....	70.8	....	24.53
<hr/>				
$C^{15}NH^{13}, HCl, HgCl$	.....	289.0	....	100.00

II.				
16 C	.....	96	....	32.54
N	.....	14	....	4.74
14 H	.....	14	....	4.74
Hg	.....	100.2	....	33.97
2 Cl	.....	70.8	....	24.01
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$C^{16}NH^{13}, HCl, HgCl$	.....	295.0	....	100.00

Stenhouse found the hydrogen too high, because mercury passed over with the water.

Hydrochlorate of sparteine produces a yellow crystalline precipitate with *terchloride of gold*. The precipitate dissolves with difficulty in water, but readily in warm hydrochloric acid, from which it separates on cooling in brilliant micaceous crystals.

*Chloroplatinate of Sparteine.*—Hydrochlorate of sparteine produces, with bichloride of platinum, an abundant yellow precipitate, which may be obtained in crystals by dissolving it in warm concentrated hydrochloric acid diluted with an equal volume of water, and leaving the solution to cool.

It forms fine, brilliant, square, prismatic crystals. (Fig. 73 without  $a$ ;  $\infty P$ .  $\infty \check{P} \infty$ .  $\infty \bar{P} \infty$ .  $\bar{P} \infty$ .  $\check{P} \infty$ .— $y : y = 105^\circ 24'$ ;  $i : i = 98^\circ 48'$ .) (Miller.) Permanent in the air. Gives off 5.54 per cent. of water, (2 atoms = 5.18 per cent.) when dried in vacuo, slowly at  $100^\circ$ , and rapidly at  $130^\circ$ — $150^\circ$ , without undergoing any further change. Decomposed by boiling with water or alcohol.

Soluble in warm hydrochloric acid, insoluble in cold water and alcohol.

I.				
15 C	.....	90	....	26.38
N	.....	14	....	4.10
16 H	.....	16	....	4.68
2 O	.....	16	....	4.73
Pt	.....	98.7	....	28.93
3 Cl	.....	106.2	....	31.18
<hr/>				
$C^{15}NH^{13}, HCl, PtCl^2 + 2Aq$	....	340.9	....	100.00

		Stenhouse.	
		<i>Dried in vacuo.</i>	
		II.	
16 C	.....	96	..... 27.67 .... 26.44
N	.....	14	..... 4.03
16 H	.....	16	..... 4.62 .... 4.87
2 O	.....	16	..... 4.61
Pt	.....	98.7	..... 28.45 .... 28.78
3 Cl	.....	106.2	..... 30.62 .... 30.64
$C^{16}NH^{13}, HCl, PtCl^2 + 2Aq$		346.9	..... 100.00

*Picrate of Sparteine.* — A cold-saturated alcoholic solution of picric acid produces a yellow precipitate on boiling with alcoholic sparteine. If the crystalline precipitate is filtered off, washed with a little hot water, and then dissolved in a large quantity of boiling alcohol, the solution deposits, on cooling, long, brilliant, brittle needles, from 1 to 2 inches long, resembling picrate of potash. Permanent in the air. Does not lose weight on drying in vacuo at  $100^\circ$ .

Explodes rather violently when heated. Heated with aqueous potash it is converted into picrate of potash and sparteine. It is but slightly soluble in alcohol, even at the boiling heat.

I.			
27 C	.....	162	.... 46.81
4 N	.....	56	.... 16.20
16 H	.....	16	.... 4.62
14 O	.....	112	.... 32.37
$C^{16}NH^{13}, C^{12}X^3H^3O^3$		346	.... 100.00

II.		Stenhouse.	
28 C	.....	168	.... 47.72 ..... 46.57
4 N	.....	56	.... 15.90 ..... 15.68
16 H	.....	16	.... 4.57 ..... 4.81
14 O	.....	112	.... 31.81 ..... 32.94
$C^{16}NH^{13}, C^{12}X^3H^3O^3$		352	.... 100.00 ..... 100.00

### *Oxyazo-nucleus* $C^{16}NH^7O^4$ .

### Apophyllic Acid.



WÖHLER. (1844.) *Ann. Pharm.* 50, 24.

TH. ANDERSON. *Edinb. Phil. Trans.* 20, 347; *Ann. Pharm.* 86, 196; *Pharm. Centr.* 1853, 187.

*Formation.* 1. By the decomposition of chloroplatinate of cotarnine (Wöhler.) — 2. By the action of dilute nitric acid upon cotarnine. (Anderson.)

*Preparation.* 1. Cotarnine is dissolved in nitric acid diluted with twice its volume of water, strong nitric acid is then added, and the whole

heated to boiling, whereupon abundance of red vapours are evolved. As soon as a small portion of the solution, on being mixed with alcohol and ether, quickly deposits crystals (if no crystals appear, the heating must be continued), the whole of the solution is treated in the same way, and the crystals which are deposited after 24 hours, are filtered off and purified by boiling their solution with animal charcoal and recrystallising. A great excess of nitric acid hinders the precipitation of the apophyllic acid. (Anderson.) — 2. On decomposing chloroplatinate of cotarnine with sulphuretted hydrogen, filtering off the sulphide of platinum and evaporating the filtrate with hydrate of baryta, apophyllate of baryta was found in the residue; and after extracting the cotarnine with alcohol and boiling the residue with dilute sulphuric acid, a yellow solution was obtained which deposited crystals of apophyllic acid after the lapse of several weeks. (Wöhler.)

*Properties.* Crystallises, on cooling its boiling saturated solution, in rather long anhydrous prisms, which do not effloresce when heated. Reddens litmus strongly, and has a weak acid taste. (Wöhler.) Melts at 205°, and solidifies into a crystalline mass on cooling. (Anderson.)

	At 100°.			Anderson.
16 C .....	96	...	53·04	..... 52·79
N .....	14	...	7·73	
7 H .....	7	...	3·86	
8 O .....	64	...	35·37	..... 4·00
<hr/>				
C <sup>16</sup> NH <sup>7</sup> O <sup>8</sup> .....	181	...	100·00	

*Decompositions.* Apophyllic acid, when heated, melts, chars, and evolves an oily, strongly alkaline liquid, which smells of chinoline. (Wöhler.) By distillation it yields a neutral oil, as well as a base which is coloured by chloride of lime. (Anderson.) — 2. It may be oxidised to oxalic acid by nitric acid. (Anderson.)

*Combinations.*—With Water. — a. *Hydrated Apophyllic acid* crystallises from a saturated and not boiling solution, in colourless, very sharp rhombic octahedrons, the form of which approaches to that of a square-based octahedron. Angles of the base about 88° and 92°. Dihedral angles, about 106° 28', 105° 24', and 190°. The crystals cleave very readily in a direction parallel to the base, forming faces of pearly lustre, like the crystals of apophyllite (hence the name).

Gives off water, amounting to about 9 per cent., at a temperature much below 100° (2 atoms = 9·04 per cent). (Wöhler.)

b. *Aqueous Apophyllic Acid.* — Apophyllic acid dissolves slowly and with great difficulty in cold water.

It is soluble in sulphuric acid. (Anderson.)

*Apophyllates.*—The apophyllates are all very easily soluble.

*Apophyllate of Ammonia* forms small prismatic needles. It is readily soluble in water.

*Apophyllate of Baryta* is obtained in nodular crystals by digesting the acid with carbonate of baryta and adding alcohol to the solution. (Anderson.)

Apophyllate of ammonia does not precipitate *lead-salts*. (Wöhler.)

*Apophyllate of Silver* is obtained by digesting apophyllic acid with moist carbonate of silver and precipitating the solution with alcohol and ether. It forms a crystalline powder, which burns slowly when heated, leaving a residue of metallic silver. It is easily soluble in water, insoluble in alcohol and ether. (Anderson.)

					Anderson.
16 C	.....	96	...	33.22	..... 32.65
N	.....	14	...	4.85	
6 H	.....	6	...	2.08	..... 2.30
Ag	.....	108.1	...	37.52	.... 37.33
8 O	.....	64	...	22.33	
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$C^{16}NH^6AgO^3$	.....	288.1	...	100.00	

*Apophyllate of Silver with Nitrate of Silver.*—Apophyllate of ammonia forms after a while, with nitrate of silver, small crystalline stars, which soon increase to groups of fine needles, resembling zeolite. It explodes violently when heated, like oxalate of silver. Slightly soluble in water.

					Anderson.
16 C	.....	96	...	20.95	..... 20.92
2 N	.....	28	...	6.11	
6 H	.....	6	...	1.30	..... 3.20
2 Ag	.....	216.2	...	47.20	..... 49.70
14 O	.....	112	...	24.44	
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$C^{16}N^2H^6Ag^2O^{14}$	....	458.2	...	100.00	

Apophyllic acid is insoluble in alcohol and in ether.

*Primary-nucleus*  $C^{16}H^{14}$ .

*Oxygen-nucleus*  $C^{16}H^{12}O^3$ .

**Camphrene**  $C^{16}H^{12}O^3$ .

J. CHAUTARD. *Compt. rend.* 44, 66; *J. pr. Chem.* 71, 310; *Chem. Centr.* 1857, 156.

*Preparation.* 250 grammes of Japanese camphor are heated with 1 kilogr. of sulphuric acid in a water-bath for 12 or 13 hours. A dark yellow solution is then formed, which is diluted with water, and the precipitated oil is washed with potash and distilled over chloride of calcium. Colourless camphrene passes over at  $240^\circ$ , amounting to about two-thirds of the product, and then, as the temperature rises, a mixture of camphrene

and camphor, which is collected separately and freed from undecomposed camphor by digesting it for two hours in a water-bath with sulphuric acid.

*Properties.* Colourless oil, which boils at 240° and does not solidify at -10°.

It does not affect polarized light. Sp. gr. = 0.974 at 6°. Has a slight aromatic odour. Vapour density = 4.517.

					Chautard.
16 C	.....	96	....	77.42	..... 77.14
12 H	.....	12	....	9.68	..... 9.64
2 O	.....	16	....	12.90	..... 13.22
<hr/>					
C <sup>16</sup> H <sup>12</sup> O <sup>2</sup>	.....	124	....	100.00	..... 100.00

		Vol.	Density.
C-vapour	.....	16	..... 6.6560
H-gas	.....	12	..... 0.8316
O-gas	.....	1	..... 1.1093
<hr/>			
Camphrene vapour	....	2	..... 8.5969
		1	..... 4.2984

*Decompositions.* 1. Camphrene is dissolved by boiling *nitric acid* with evolution of nitrous acid. Water precipitates from the solution a soft uncrystallisable resin, soluble in alcohol. Neither camphor nor camphoric acid is formed in this reaction. — 2. It is coloured red by fuming *sulphuric acid*, but no combination takes place. — 3. Fused with *hydrate of potash*, out of contact with the air, it forms a mass which solidifies on cooling and from which a yellow resin may be extracted. This latter does not yield camphor by distillation.

*Oxygen-nucleus* C<sup>16</sup>H<sup>10</sup>O<sup>4</sup>.

**Cholesteric Acid.**



REDTENBACHER. (1846.) *Ann. Pharm.* 57, 145.

SCHLIEPER. *Ann. Pharm.* 58, 385.

GUNDELACH & STRECKER. *Ann. Pharm.* 62, 226.

*Formation.* By the action of nitric acid: 1. upon choloïdic acid, 2. upon cholesterin (Redtenbacher); 3. upon cholic acid (Schlieper); 4. upon hyocholic acid. (Gundelach & Strecker).

*Preparation.* 1. The residue which, on treating choloïdic acid with nitric acid, remains in the retort after the volatile products have distilled off, consists of crystalline choloïdanic acid and a yellowish brown acid liquid, containing oxalic acid, cholesteric acid, nitric acid, and a soft resin. This liquid is filtered from the choloïdanic acid through



powdered glass, then diluted with water and filtered from the soft resin; and the filtrate is evaporated down, again diluted with water, again evaporated down, &c, until the soft resin is separated. The solution is neutralised with ammonia, precipitated with an excess of nitrate of silver and boiled. Oxalate of silver is then precipitated, while cholesterate of silver remains in solution, and is obtained in crystals after the boiling filtered solution has cooled. The silver-salt is suspended in water and sulphuretted hydrogen passed through; the whole is then warmed, filtered, and the filtrate evaporated: the cholesteric acid is thereby obtained as a gummy mass. (Redtenbacher.)

2. From *Cholesterin*. Cholesterin is distilled with moderately strong nitric acid, and the distillate repeatedly poured back as long as the action continues. Water is finally poured into the retort in order to carry over all the volatile acids, and the residue is diluted with water, which separates a small quantity of resin. The filtered solution yields cholesteric acid on evaporation. (Redtenbacher.)

3. From *Cholic acid*. When cholic acid is heated with nitric acid in a retort, a violent reaction takes place accompanied by strong frothing and evolution of red vapours; the liquid is then boiled—in case of oily drops which solidify on cooling, continuing to swim upon the liquid—for five or six days, or until all evolution of nitrous acid has ceased; and the remaining yellowish solution is evaporated on a water-bath. It then deposits a transparent yellowish gum, which may be separated from undecomposed cholic acid by repeated solution in water, filtering and evaporating, until the residue dissolves without turbidity. In this process, neither volatile acids nor oxalic acid are formed. (Schlieper.)

4. From *Hyochohic acid*. Hyochohic acid is distilled with fuming nitric acid as long as nitrous acid continues to be evolved; the residual liquid is diluted with a large quantity of water, then decanted from the resinous matter, concentrated, and saturated with ammonia, which causes a red coloration. It is then rapidly evaporated and mixed with alcohol, whereupon it gradually deposits crystals of oxalate of ammonia. The mother-liquor, mixed with more alcohol, deposits nitrate of ammonia; chloride of calcium is then added, which produces a rust-brown gelatinous precipitate of cholesterate of lime. The precipitate is obtained of a lighter colour by washing it with dilute alcohol and repeatedly dissolving it in water and reprecipitating with alcohol. It is finally converted into cholesterate of silver by precipitating the aqueous solution with nitrate of silver. (Gundelach & Strecker.)

*Properties.* Cholesteric acid is deposited by evaporation from its aqueous solution as a gummy light yellow mass, which remains soft in the interior. It has a rather acid and strongly bitter taste. (Redtenbacher.)

*Decompositions.* When heated in small tubes it evolves a brown, suffocating, bitter vapour, and leaves a residue of charcoal. Burns in the air with a smoky flame. (Redtenbacher.)

*Combinations.* Cholesteric acid becomes soft in moist air. It dissolves readily in water and forms a yellow solution.

The cholesterates of the alkalis and alkaline earths do not crystallise; they dissolve in water. (Redtenbacher.)

*Cholesterate of Lime.* — The lime-salt, prepared according to 4, gave,

when dried at 100°, 24·2 per cent. CaO, 89·7 C, and 5·4 H. ( $C^{16}Ca^3H^8O^{10}$  requires 25·0 per cent. CaO, 42·4 C, and 8·6 H.)

It dissolves readily in cold water and is precipitated by boiling. After the solution has been exposed to the air for two months, it is precipitated by acids in brown flakes. The aqueous solution is precipitated by alcohol. (Gundelach & Strecker.)

The alkaline cholesterates form yellowish precipitates with salts of the metals; they precipitate ferric salts yellowish brown, and cupric salts yellowish green. (Redtenbacher.)

*Cholesterate of Silver.* — *Preparation* (p. 158). Or cholesterate of lime, obtained according to 4, is precipitated with nitrate of silver, whereby yellow flakes are formed. (Gundelach & Strecker.)

In order to obtain the silver-salt crystallised, the liquid is mixed with a little nitrate of ammonia, which acts as a solvent, and boiled, the greater part then dissolving. The solution is filtered boiling, and, on cooling and concentrating the mother-liquors, yellowish granular crystalline crusts are obtained. (Schlieper, Gundelach & Strecker.)

				Redtenbacher.		
				a.	b.	
<i>Dried at 100°.</i>						
16 C .....	96	...	23·99	.....	23·70	... 23·90
8 H .....	8	...	1·99	.....	2·23	... 2·31
8 O .....	64	...	15·99	.....	15·82	... 16·28
2 AgO .....	232·2	...	58·03	.....	58·25	... 57·51
<hr/>						
$C^{16}Ag^2H^8O^{10}$ .....	400·2	...	100·00	.....	100·00	... 100·00

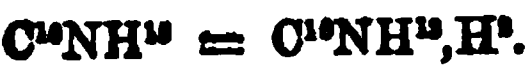
				Schlieper.	Gundelach & Strecker.	
<i>Dried at 100°.</i>						
16 C .....	96	...	23·99	.....	23·81	... 24·1
8 H .....	8	...	1·99	.....	2·35	... 2·4
8 O .....	64	...	15·99	.....	16·14	... 15·8
2 AgO .....	232·2	...	58·03	.....	57·70	... 57·7
<hr/>						
$C^{16}Ag^2H^8O^{10}$ .....	400·2	...	100·00	.....	100·00	... 100·0

a was obtained from choloidic acid, b from cholesterin.

Cholesteric acid is readily soluble in alcohol and forms a yellowish solution. (Redtenbacher.)

*Aso-nucleus*  $C^{16}NH^{13}$ .

Conine.



A. L. GISEKE. (1827.) *Br. Arch.* 20, 97.  
R. BRANDES. *Br. Arch.* 20, 111.  
TROMMSDORF. *N. Tr.* 12, 2, 49. .  
GRIGER. *Mag. Pharm.* 85, 72, and 259.

LIEBIG. *Mag. Pharm.* 36, 159.

BOUTRON-CHARLARD & O. HENRY. *Ann. Chim. Phys.* 61, 337; *J. Pharm.* 22, 277.

ORTIGOSA. *Ann. Pharm.* 42, 813.

BLYTH. *Chem. Soc. Qu. J.* 1, 345; *Ann. Pharm.* 70, 73.

A. W. HOFMANN. *Ann. Pharm.* 74, 175.

V. PLANTA & A. KÉKULÉ. *Ann. Pharm.* 89, 129.

WERTHEIM. *Ann. Pharm.* 100, 335; *Pharm. Centr.* 57, 41.

*Conicine.* (Berzelius.) *Coniine.*

Conine was obtained by Giseke (1827) as an impure sulphate, pure by Geiger (1831), and recognised by him as an organic alkali; his views were opposed by Deschamps (*J. Pharm.* 21, 74; 22, 231), but confirmed by Boutron-Charlard, and O. Henry.

*Sources.* From the herb and seed of *Conium maculatum*. — Also from the flowers of that plant. (Wertheim.)

*Formation.* By heating conydrin with anhydrous phosphoric acid. (Wertheim.) — By treating the alcoholic extract of imperatoria-root with potash, Wagner obtained a volatile base, which he believes to be conine. (*J. pr. Chem.* 61, 504.)

*Preparation.* 1. The seeds of hemlock are distilled with carbonate of potash or hydrate of lime, and the yellowish distillate, upon which oily drops float, is neutralised with sulphuric acid and evaporated; it then becomes first red, then violet, and lastly brown, and deposits brown resinous flakes, which are separated by filtration. The filtrate is evaporated to the consistence of a thick syrup, and the residue is treated with a mixture of three parts absolute alcohol and one part ether, as long as it continues to grow turbid. A precipitate of sulphate of ammonia is thus formed, from which the liquid is filtered and then distilled; and the residue is heated in a water-bath and repeatedly moistened with water, until no more alcoholic vapours are perceptible. On cooling, the mass is found to contain a number of micaceous laminae, which cannot be separated. The whole is therefore distilled with potash in a chloride of calcium bath, whereupon a clear yellowish oil first passes over, containing alcohol (probably from sulphovinate of potash) and smelling strongly of conine. If this product is rendered turbid by mixture with the following distillate, the receiver must be changed, and the distillation continued till the residue is almost dry, when it is again to be mixed with caustic potash and water, and distilled as long as conine continues to pass over. The distillate, consisting of a watery liquid and oily conine, which still contains water in solution (whence it becomes turbid when heated) is mixed with chloride of calcium as long as the latter continues to absorb water, and then distilled; ammonia is then evolved, and there remains a brown resinous residue. The distillate is again treated with chloride of calcium and distilled in a sand-bath, and the product, which is almost colourless, is rectified alone: it then leaves a small resinous residue. (Geiger.) 6 lbs. fresh green unripe seeds, or 9 lbs. dry ripe seeds, yield 1 oz. conine. (Geiger.) The herb of hemlock yields but a small product; the seeds yield more. The latter contain a neutral oil, which is previously separated by distilling the seeds with water containing sulphuric acid; — it passes over

partly in dirty white flakes and partly in aqueous solution. Hydrate of magnesia may be also used for the separation of conine. (B.-Charlard & Henry.)

2. The ripe seeds are exhausted with alcohol, the alcohol is distilled off, and the residual syrup is mixed with an equal volume of water, and a little hydrate of potash, and distilled in a chloride of calcium-bath. (Christison.)

3. When the fresh flowers (or seeds) of hemlock are exhausted with hot water to which a little sulphuric acid has been added, and the extract supersaturated with lime or hydrate of potash and distilled as rapidly as possible, a strongly alkaline distillate containing ammonia, conine, and conhydrine passes over. The distillate is neutralised with sulphuric acid, evaporated on a water-bath to a thick syrupy consistency, and then treated with absolute alcohol, which precipitates sulphate of ammonia. The solution is removed from the deposit and placed on a water-bath in order to evaporate off the alcohol; and the residue is allowed to cool, then strongly supersaturated with concentrated potash and mixed with ether, the whole being shaken for a considerable time. The brownish red ethereal solution thus obtained is separated from the aqueous solution and evaporated on a water-bath, till the ether is completely driven off; it is finally heated to  $100^{\circ}$ , and then distilled in a stream of hydrogen, at a very slowly increasing temperature, in an oil-bath. Conine, rendered impure by a little water and ether, first passes over, and afterwards colourless oily conine, which may easily be purified by neutralising with hydrochloric acid, pouring off the mother-liquor from the crystals of hydrochlorate of conine, and recrystallising the salt from alcohol. Conhydrine remains in the retort and, on heating, sublimes in the upper part and neck of the retort in crystalline laminæ (if very slowly heated, it sublimes at  $150^{\circ}$ , otherwise between  $190^{\circ}$  and  $210^{\circ}$ ). (Wertheim.)

*Purification of Conine.* Conine, obtained by Geiger's process, may still contain ammonia. To remove this impurity, the product is shaken in a long glass tube with water, and, after a few hours, the conine is decanted off. The wash-water becomes milky on being shaken up with chlorine-water, but does not evolve nitrogen gas, if free from ammonia. (B.-Charlard & Henry.) The ammonia is removed by placing the conine in vacuo over sulphuric acid, the evolution of gas bubbles then causing ebullition. (Liebig.) If the conine contains water, it is to be mixed with fused hydrate of potash: the conine then separates out, after a time, in an oily stratum, which may be removed and rectified alone. Commercial chloride of calcium cannot be used for this purpose, as it generally contains alumina. Conine, from different preparations, does not always behave in the same way with hydrate of potash; in one instance, the addition of potash caused a violent evolution of ammonia and decomposition. (Blyth.) When conine, from another preparation, was allowed to stand for two days over hydrate of potash, then poured off and distilled in a stream of hydrogen, it began to boil at  $97^{\circ}$ , and, while the boiling point rose to  $132^{\circ}$ , a limpid oil passed over, which contained but little conine, and formed crystals with bromine. The boiling point then rose rapidly to  $170^{\circ}$ , and pure conine distilled over up to  $175^{\circ}$ , after which came products of decomposition. The oil which passed over between  $170^{\circ}$  and  $175^{\circ}$  became turbid when heated to  $50^{\circ}$ , and deposited water in the neck of the retort. On treating it with potassium, it evolved gas violently, while

potash was formed, and on subsequently distilling the liquid in a stream of hydrogen it passed over between  $168^{\circ}$  and  $170^{\circ}$ . (Blyth.)

**Properties.** Conine is a limpid oily liquid of sp. gr. 0.89 (Geiger), 0.878. (Blyth.) It boils at  $168^{\circ}$  —  $171^{\circ}$  (Blyth); at  $187.5^{\circ}$  (Geiger);  $189^{\circ}$  (Christison);  $212^{\circ}$  (Ortigosa); and when carefully but rapidly heated, distils almost without decomposition. (Geiger.) It volatilises in vacuo at ordinary temperatures, and distils without residue. (Liebig, Ortigosa.) It may be carried over with vapour of water at  $100^{\circ}$ , but even then slight decomposition takes place. — It has a highly penetrating, repulsive, peculiar and suffocating odour, like tobacco, somewhat resembling also that of hemlock; at a distance, and in small quantity, it smells like mice, but if closely inhaled, it attacks the head and provokes tears. (Geiger.) It has a very sharp, repulsive, tobacco-like, and persistent taste. It is a violent poison, and in small quantities rapidly causes death, attended with tetanus. When outwardly applied it does not dilate the pupil, not even if introduced into the eye itself. (Geiger.) (On the action of conine compare Christison, *J. Pharm.* 22, 413; *J. Ch. Med.* 12, 461. Köhlmann, *N. Br. Arch.* 23, 38.) It has a strong alkaline reaction, but only in the presence of water. (Geiger.) The alkaline reaction disappears from turmeric paper on application of heat, and slowly from litmus-paper. (Blyth.)

					Ortigosa.		Blyth.
16 C	.....	96	....	76.80	.....	74.59	.... 75.11
N	.....	14	....	11.20			
15 H	.....	15	....	12.00	.....	12.05	.... 13.06
<hr/>							
$C^{16}NH^{15}$	.....	125	....	100.00			

Liebig found 66.91 C, 12.0 H, 12.8 N, and 8.29 O, and gave the formula  $C^{13}NH^{14}O$ , which Ortigosa changed to  $C^{16}NH^{16}$ , Blyth to  $C^{17}NH^{17}$ . Gerhardt (*Compt. Chim.* 1849, 373) gave the above formula, and considered it probable that Ortigosa and Blyth analysed conine containing water. According to v. Planta and Kekulé, conine is generally a mixture of  $C^{16}NH^{15}$  and  $C^{18}NH^{17}$  (methyl-conine), and perhaps also contains the base  $C^{14}NH^{13}$ ; they are of opinion, that Blyth's conine contained methyl-conine.

**Decompositions.** 1. Conine is very inflammable, and burns with a bright smoky flame, like volatile oils, leaving only a small residue of carbon. (Geiger.) The vapour of conine is inflammable. (Charlard & Henry.)

2. Conine remains colourless when kept from the air, but on exposure to the air, it rapidly turns yellow, brown, and viscid, and becomes less soluble in water. The aqueous or alcoholic solution undergoes the same decomposition, especially if the conine is impure; both rapidly turn brown, while the aqueous solution becomes turbid and deposits resinous flakes. (Geiger.) In the decomposition of conine by the air, resin is formed and ammonia evolved. (Christison.) Conine, placed in a shallow dish and exposed to the action of oxygen for some weeks, turns dark red, becomes thicker, and is finally converted into a stringy resinous mass, which smells strongly of conine and has an alkaline reaction. This resin dissolves in strong hydrochloric acid and is precipitated by carbonate of potash. If this operation is repeated and the product washed with water, a resin is obtained which is free from conine, smells of butyric acid when burnt or exposed to moist air, and contains nitrogen. (Blyth.)

3. On *distilling* conine, a portion is always decomposed, ammonia

being evolved and a resin formed. The purer the conine, the less decomposition takes place. Heated for some time to a temperature near its boiling point, it is much more decomposed than when it is rapidly heated to boiling, in which case the greater part distils over unchanged. Ammonia and a resin are formed, and perhaps also carbonic and acetic acids. (Geiger.) Moist conine, evaporated in vacuo over substances which attract moisture, leaves a resinous pitchy residue. (Charlard & Henry.) Moist conine leaves a resin on distillation; the dry substance does not. (Ortigosa.) When conine is heated above  $172^{\circ}$ , the boiling point rises rapidly, decomposition takes place, and white fumes are evolved. (Blyth.)

4. In the *oxidation* of conine, butyric acid is generally formed, as when conine is boiled with nitric acid (a resin is formed at the same time, which is precipitated from the solution by potash on cooling); also on evaporating bromide of conine in vacuo with a slight excess of bromine, or by evaporating sulphate of conine to dryness, and by treating conine with bichromate of potash and sulphuric acid. (Blyth.) An odour of butyric acid is perceptible during the evaporation of the platinum or mercury salts of conine, and of its basic substitution-products. (v. Planta & Kekulé.)—Conine reduces silver-salts. (Ortigosa.)

5. When conine is neutralised with dilute mineral *acids*, it is not decomposed by spontaneous evaporation, but if evaporated with the aid of heat, its solution becomes dark, and a salt of ammonia and a resin are formed. The same reaction is produced, even in the cold, by an excess of acid, or by acetic or tartaric acid. (Geiger.)

6. Alcoholic *tincture of iodine* acts violently upon moist conine, the solution becoming turbid and yellow for a few moments, and then colourless, and ultimately drying up to an uncrystallisable mass. (Geiger.) A weak tincture of iodine added drop by drop to alcoholic conine, produces a dark brown precipitate which dissolves and forms a colourless liquid. When tincture of iodine is added as long as the liquid remains colourless (if an excess of iodine is added a different decomposition takes place), and the solution is evaporated in vacuo, there remains a brownish mother-liquor containing crystals of a similar form to those obtained by the action of bromine upon conine: they are readily soluble in water, alcohol, and ether. (Blyth.)—Anhydrous conine becomes heated in contact with iodine, and forms thick white fumes and a readily fusible mass, which is at first blood-red and afterwards turns olive-green; this body dissolves in water, forming a nearly colourless solution, and depositing a black thick resin. (Geiger.)

7. When conine (distilled at  $169^{\circ}$ ) is exposed to vapour of *bromine*, it immediately solidifies into a mass of crystalline needles. If too much bromine is used, the chief product is a gummy mass; if conine is employed which distils over below  $168^{\circ}$ , a red liquid is formed. The purer the conine, the more abundant is the formation of crystals. Conine which has passed over between  $98^{\circ}$  and  $136^{\circ}$  does not at first form any crystals with bromine, and on evaporating in vacuo, becomes dark red or, if more bromine is added, black. This product, dissolved in water, boiled with animal charcoal, then filtered and evaporated in vacuo over sulphuric acid, yields transparent colourless needles and a brown mother-liquor. The crystals, after washing with ether, contain 48.52 per cent. C. and 8.98 H.; they are readily soluble in water and in alcohol, but much less in ether; when purified by treating with ether and recrystallised from water or from alcohol, they form needles which are permanent in the air



and melt into an oil at about  $100^{\circ}$ , giving off a little conine vapour. On cooling, the oil solidifies into a striated mass. (Blyth.)

8. Anhydrous conine acted upon by *chlorine gas* gives off dense white fumes, becomes hot and thick, and forms a brown mass, which has a peculiar odour something like that of chlorine, but not like that of conine, and when suspended in water and treated with caustic soda, diffuses an odour of conine and turpentine. — With hydrated conine, chlorine gas produces a whitish turbidity, separation of oil-drops, and a smell of chloride of nitrogen; if potash is then added, an odour of conine is evolved. (Geiger.) Moist conine, free from ammonia, does not evolve nitrogen when shaken with chlorine-water. (Charlard & Henry.) When chlorine gas is passed over conine which has distilled at  $130^{\circ}$ , the conine becomes hot, assumes a dark red colour, and emits heavy white vapours which smell something like oil of lemons. If the action of the chlorine be continued and the oil cooled, it becomes colourless again and thicker, ceases to evolve white vapours, and becomes covered with white crystals, into which it is completely converted after the chlorine has been passed over it for a long time. The crystals are like those formed by the action of bromine, and are very volatile. If stirred up with water they readily dissolve; they are very soluble in alcohol and ether, from which they crystallise.

9. Anhydrous conine poured upon dry *chromic acid*, takes fire immediately. (Hofmann, *Ann. Pharm.* 47, 85.)

10. *Phosphomolybdic acid* (obtained by precipitating molybdate of ammonia with common phosphate of soda, evaporating the solution to dryness, igniting till the ammonia is driven off, and dissolving the residue in water containing nitric acid) forms with conine and its salts, a bright yellow bulky precipitate. The precipitate is scarcely soluble at the ordinary temperature in water, dilute acids (with the exception of phosphoric acid), alcohol, or ether; it is however readily taken up by the carbonates, borates, and phosphates of the alkalis, and decomposed, though more slowly and with separation of conine, by the alkaline earths and their carbonates, as well as by the oxides of lead and silver and their carbonates. (Sonnenschein, *Ann. Pharm.* 105, 45.)

11. Conine is rapidly attacked by *bromide of ethyl* and forms a crystalline product. (Hofmann, *Ann. Pharm.* 74, 175; 79; 31.) Commercial conine mixes with iodide of ethyl, and forms at first a clear liquid; but a reaction quickly takes place, whereby a brown oil is formed, which sinks to the bottom of the vessel. If the mixture is heated in a sealed tube to  $100^{\circ}$ , till the stratum of ether at the bottom no longer decreases, there is formed, if the conine is pure, a viscid oil (hydriodate of ethyl-conine); but if the conine contains methyl-conine, there is formed, besides hydriodate of ethyl-conine, the hydriodate of ethyl-methyl-conine, which solidifies in part immediately, and completely on cooling. (v. Planta & Kekulé.)

12. With *cyanide of ethyl* conine behaves like aniline. (Wurtz, *Ann. Pharm.* 80, 349.)

*Combinations.* Conine takes up at ordinary temperatures one-third part of its weight of water, and at a low degree of cold, one part of water, whereby it becomes more fluid. It then becomes turbid when heated, owing to the separation of water. (Geiger.) It is slightly soluble in water. (Charlard & Henry.) The solution in 100 parts of cold water, becomes turbid when heated and clear again on cooling. (Geiger.)

Conine does not appear to dissolve *phosphorus*. It dissolves *sulphur* in large quantities, and the dark orange-coloured solution yields crystals of sulphur on evaporation. It is slightly soluble in *bisulphide of carbon*. (Blyth.)

Conine neutralises acids completely. (Geiger, Charlard & Henry.) It produces white fumes with volatile acids (with hydrochloric acid, Charlard & Henry), also with nitric acid and acetic acid (Blyth), probably from the ammonia contained in it. (Geiger.) It appears to drive out ammonia from its compounds, and precipitates stannous, mercurous, and ferric salts (Ortigosa); also the salts of alumina, zinc, manganese, copper, and silver; oxide of silver dissolves in an excess of conine. (Blyth.)

The *salts of conine* cannot for the most part be obtained in the crystalline form. (Geiger.) A few crystallise, but they are very deliquescent. (Blyth.) They are less poisonous (still more poisonous, according to Christison) than conine itself; they have a repulsive bitter taste, and decompose with excess of acid on exposure to the air, turning red, then violet, and afterwards green. (Geiger.) Conine turns bluish green, and afterwards brownish red, even while it is being saturated with acids. (Charlard & Henry.) Many of its salts decompose on evaporation and leave a gummy residue (Blyth), part of the base volatilising. (Charlard & Henry.) All compounds of conine when burnt emit the repulsive odour of conine. (Blyth.) The salts of conine dissolve readily in water (Geiger), and in alcohol. (Charlard & Henry.) They are precipitated by tannin. (Geiger.)

Conine forms a crystallisable salt with *phosphoric acid*. (Charlard & Henry.)

*Sulphate of Conine*. — Conine neutralised with sulphuric acid dries up in the air to a brown extract, which cannot be obtained crystallised, and dissolves in water in all proportions. (Geiger.) Conine forms with sulphuric acid a crystallisable, deliquescent salt, which dissolves in alcohol in all proportions. (Charlard & Henry.) Conine neutralised with dilute sulphuric acid and evaporated on a water-bath, becomes brownish, and leaves a thick gummy residue containing traces of crystals. Potash separates from the residue an oil which smells like unaltered conine; if the evaporation is carried further, the same substance is produced as by bromine. (Blyth.)

Conine dissolved in alcohol of 30° forms with *iodic acid* a precipitate similar to those produced by many other organic bases. (Charlard & Henry.)

*Hydrochlorate of Conine*. — Conine behaves with hydrochloric acid in the same manner as with sulphuric acid. (Geiger.) When conine is placed in vacuo beside a vessel containing fuming hydrochloric acid, crystals are formed in both the liquids, which finally solidify into a mass of large crystalline laminae. The crystals in both vessels are the same in form and appearance, yet those from the conine vessel have an alkaline, those from the hydrochloric acid vessel an acid reaction. (Liebig.) Conine neutralised with hydrochloric acid turns pale red and yields crystals when the solution is evaporated nearly to dryness. (Blyth.) Conine (even crude) mixed with hydrochloric acid yields crystals easily and rapidly. (Wertheim.)



Colourless needles (Liebig), long white needles grouped in stars. (Blyth.) Transparent rhombic crystals, having a fatty lustre and softer than gypsum, sometimes four millimeters long. (Fig. 68 without  $i$  and  $p$ ; sometimes fig. 53 without  $i$  and  $p$ .  $\infty \bar{P} \infty . \bar{P} \infty . \infty P$ , sometimes with  $\infty \bar{P} \infty$  and  $m P n$ . (Peters.)

Permanent in the air (Wertheim); deliquescent. (Liebig, Blyth.) When the solution obtained by the deliquescence of the salt is evaporated at a gentle heat, it again yields the same crystals; but the liquid, if evaporated in the air, turns first purplish red, then deep indigo-blue, and finally brown. — Hydrochloric acid gas passed over conine, turns at first purple-red and then deep indigo-blue. (Liebig.)

					Wertheim.
16 C	.....	96	....	59.44	..... 58.86
N	.....	14	....	8.67	
16 H	.....	16	....	9.91	..... 10.05
Cl	.....	35.5	....	21.98	..... 21.52
<hr/> $C^{16}NH^{16}, HCl$					<hr/> ..... 161.5 .... 100.00

The salt was prepared with conine obtained from conhydrine by the action of anhydrous phosphoric acid,

*Nitrate of Conine.* — Conine neutralised with nitric acid becomes turbid at the point of neutralisation, and rapidly clear on the addition of more acid. The neutral mixture smells feebly of conine, and when left to evaporate, or evaporated at a temperature between  $30^{\circ}$  and  $40^{\circ}$ , leaves an extract-like residue, containing colourless, transparent octohedrons. (Geiger.) It is crystallisable. (Charlard & Henry.)

Aqueous conine shaken with *phosphate of magnesia* forms a white insoluble salt. (Charlard & Henry.)

When conine is mixed with aqueous *sulphate of alumina*, small octohedrons are gradually formed, which, after being carefully washed with water, turn black on ignition. (Ortigosa.)

Conine forms with *sulphate of copper* a precipitate which dissolves slightly in water and readily in alcohol and in ether. (Ortigosa.) With *protochloride of tin*, it forms a light kermes-brown precipitate. (v. Planta.)

*Chloromercurate of Conine.* — Conine forms with corrosive sublimate a white pulverulent precipitate, which turns yellow and decomposes at  $110^{\circ}$ ; it is insoluble in water, alcohol, and ether. (Ortigosa.) When conine which has passed over between  $147^{\circ}$  and  $160^{\circ}$  and has become brown from exposure to the air, is rectified, and the colourless distillate is dissolved in alcohol, a copious precipitate is formed on addition of an alcoholic solution of corrosive sublimate. This precipitate if stirred up unites into a light lemon-coloured, viscid mass, which gradually hardens on exposure to the air, and may then be pulverised. Aqueous corrosive sublimate produces with an alcoholic solution of conine which has distilled over at  $169^{\circ}$ , a precipitate which is the same in composition but is not viscid.

Pale lemon-coloured powder, which, when heated to  $32^{\circ}$  or in vacuo over sulphuric acid, evolves an odour of conine. Melts and decomposes at  $100^{\circ}$ . Insoluble in water. Dissolves in hydrochloric acid, and is depo-

sited from the solution, on evaporation, as a gummy mass. Sparingly soluble in alcohol, insoluble in ether. (Blyth.)

					Blyth.
16 C	.....	96	....	14.40	..... 15.91
N	.....	14	....	2.10	
15 H	.....	15	....	2.25	..... 2.68
4 Hg	.....	400	....	60.00	..... 59.17
4 Cl	.....	141.6	....	21.25	..... 18.87
<hr/>					
$C^{16}NH^{15}, 4HgCl$	.....	666.6	....	100.00	

*Iodomercurate of Potassium* forms with conine a precipitate insoluble in hydrochloric acid. (v. Planta.)

From *nitrate of silver* conine precipitates oxide of silver, which redissolves in an excess of conine. (Blyth.)

*Chloride of Silver* dissolves in conine as in ammonia. (Blyth.)

*Terchloride of Gold* forms a yellow powder with conine. (Blyth.)

*Chloroplatinate of Conine.* — A solution of bichloride of platinum is added to an alcoholic solution of conine. (Ortigosa.) — When colourless conine, which has distilled over between  $106^{\circ}$  and  $136^{\circ}$  (or between  $160^{\circ}$  and  $171^{\circ}$ ), is neutralised with hydrochloric acid, and alcohol and then alcoholic bichloride of platinum are added, the liquid turns dark red and becomes oily, but does not deposit any precipitate. If evaporated in vacuo over sulphuric acid, it yields tufts of crystals. The mother-liquor deposits no more crystals on further evaporation, but evolves hydrochloric acid and an odour of butyric acid; but on mixing it with water and evaporating over sulphuric acid, more crystals are obtained. (Blyth.)

Beautiful orange-yellow crystalline powder. (Ortigosa.) Deep scarlet, four-sided prisms terminating in four-sided pyramids. It does not decompose at  $100^{\circ}$ , but melts at a few degrees higher and evolves vapour of conine. It is decomposed by potash in the cold. (Blyth.) Soluble in water (Ortigosa); slightly in cold water. (Blyth.) Soluble in alcohol and in ether. (Ortigosa). Crystallises from its solution in boiling alcohol on cooling. (Blyth.) Fig. 80 with  $\gamma$  and  $\alpha$ .  $\infty \bar{P} \infty . \bar{P} \infty . oP . \bar{P} \infty . \infty P . 3P2 . \alpha \bar{P} . P$ . (Peters.)

					Ortigosa.	Blyth.
16 C	.....	96	....	28.98	..... 29.04	..... 29.77
N	.....	14	....	4.22	..... 4.62	..... 4.05
16 H	.....	16	....	4.83	..... 5.01	..... 5.16
Pt	.....	99	....	29.89	..... 29.38	..... 29.08
3 Cl	.....	106.2	....	32.08	..... 31.95	
<hr/>						
$C^{16}NH^{15}, HCl, PtCl^2$	.....	331.2	....	100.00	.....	100.00

Conine which has become coloured by exposure to the air, gives with bichloride of platinum, black crystals, which, after they have been washed with alcohol, contain 30.43 per cent. of platinum, and give off an odour of conine when treated with potash; hence they are chloroplatinate of conine mixed with another body. (Blyth.)

The red salt boiled with a solution of bichloride of platinum gives

off carbonic acid and emits at first the odour of some fatty substance, then, while the solution becomes darker, an odour of butyric acid, and finally again the odour of the fatty substance; platinum is also reduced, and a little oil, which becomes semi-fluid on cooling, passes over. — If the mixture is boiled for about four weeks and finally evaporated to dryness, and the black residue then boiled with water and filtered from the reduced platinum, a mixture of substances is obtained on evaporating the filtrate, consisting principally of yellow octohedrons of chloroplatinate of ammonium, long four-sided purple prisms (doubtless the ammonio-protochloride of platinum of Magnus), and white silky needles, besides a little undecomposed platinum-salt. The white crystals appear to be acid; they dissolve in potash, from which they may be precipitated by acids. They are also obtained, together with the black crystals, when conine which has become coloured in the air, is treated with bichloride of platinum. If the whole mixture of crystals is treated with cold potash and the liquid diluted, rapidly filtered, and washed with water, there remains a residue of chloroplatinate of ammonium, while the purple and white salts dissolve. On evaporating the purplish red potash-solution, red four-sided prisms, insoluble in alcohol, are again obtained together with white crystals. The red crystals are Magnus's chloroplatinite of potassium; they crystallise out when the mixture of red and white crystals is dissolved in water and mixed with alcohol; they leave a colourless mother-liquor. When chloroplatinate of conine is mixed with a little water in a tube, and heated for a short time to  $140^\circ$ , it dissolves; the liquid then becomes dark and deposits platinum, and if evaporated after it has been filtered, does not yield any crystals. Treated with potash it evolves an odour of conine; hence chloroplatinite of conine seems to have been formed. (Blyth.)

Conine forms with *oxalic acid* a salt which crystallises in prisms. (Charlard and Henry.)

Conine neutralised with *acetic acid*, forms a brown, uncrystallised, varnish-like, gelatinous mass, which is inodorous, has a bitter and sharp taste, and is neutral; it dissolves in water and deposits yellowish brown, resinous flakes. (Geiger.)

On neutralising *tartaric acid* with conine, ( $2\frac{1}{4}$  grains of conine require  $1\frac{1}{2}$  grains of acid) the liquid turns brownish, becomes turbid, and then green, and exhibits an acid reaction. On evaporating, resinous flakes are deposited, but no crystals are obtained. (Geiger.)

Conine is very readily soluble in *alcohol*. 1 part of conine dissolved in 4 parts of alcohol, mixes with water in every proportion. A solution of 1 part of conine in 1 part of absolute alcohol mixes with 1 part of water, but if more water is added, the liquid becomes permanently turbid.

It is readily soluble in *ether*, and in *oils* both volatile and fatty (Geiger), also in *acetone*. (Blyth.)

*Tincture of Galls* produces with solutions of conine and its salts, a grey flocculent precipitate. The precipitate obtained with tannin is white, curdy and voluminous, and dissolves in alcohol. (B.-Charlard & Henry.)

## Conhydrine.



TH. WERTHEIM. *Wien. Acad. Ber.* 22, 113; *Pharm. Centr.* 1857, 41; *Ann. Pharm.* 100, 328.

*Source.* In the flowers and ripe seeds of *Conium maculatum*.

*Preparation* (p. 16). Conhydrine is purified from adhering conine by pressing the product after it has been submitted to a low temperature (by means of a freezing mixture), and subsequently by repeated recrystallisation from ether. (100 kilogr. of fresh flowers yield 6 grammes of pure crystals.)

*Properties.* Conhydrine crystallises in laminæ having a pearly lustre and splendid iridescence; they melt at a gentle heat and sublime below 100°. It has a slight odour, which increases when the substance is volatilised, and closely resembles that of conine. Its aqueous and alcoholic solutions have a strong alkaline reaction. Its physiological action is narcotic, but less powerful than those of conine. (0·3 gramme administered to a full-grown rabbit produced symptoms of poisoning, such as hurried breathing and dragging of the hind legs, which lasted for an hour, after which the animal began to recover.)

*Decompositions.* 1 part of conhydrine heated to 200° for an hour and a half with 3 pts. of anhydrous phosphoric acid in a glass tube, decomposes into conine and water.

*Combinations.* Conhydrine is rather soluble in water.

It neutralises acids, drives out ammonia from its compounds, but appears to be separated from its salts by conine.

*Hydrochlorate of Conhydrine.* — Conhydrine neutralised with hydrochloric acid cannot be made to crystallise.

*Chloroplatinate of Conhydrine.* — An alcoholic solution of conhydrine neutralised with hydrochloric acid is mixed with alcoholic bichloride of platinum, care being taken to avoid an excess of the latter, and the whole is placed over sulphuric acid in vacuo; when crystals begin to form, the solution is removed to the air and allowed to evaporate, and the crystals are washed, first with ether-alcohol, then with ether. The salt crystallises in hyacinth-red tablets, from 1 to 4 millim. in length, belonging to the right prismatic system.

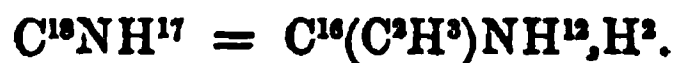
<i>Dried at 100°.</i>				Wertheim. (mean.)	
16 C	.....	96	... 27·47	.....	27·58
N	.....	14	... 4·01	.....	4·55
18 H	.....	18	... 5·15	.....	5·31
Pt	.....	99	... 28·33	.....	28·04
38 Cl	.....	106·2	... 30·47		
2 O	.....	16	... 4·57		

---

$\text{C}^{16}\text{NH}^{17}\text{O}^2, \text{HCl}, \text{PtCl}_2$  ... 849·2 ... 100·00

*Conjugated compounds containing a nucleus derived from  $C^{16}NH^{13}$ .*

### Methyl-conine.



V. PLANTA & KEKULÉ. (1854.) *Ann. Pharm.* 89, 144; *Pharm. Centr.* 1854, 280.

Methyl-conine is generally, together with conine ( $C^{16}NH^{15}$ ), one of the component parts of commercial conine; whence, on treating the latter with iodide of ethyl, ethyl-methyl-conine is formed as well as ethyl-conine.

It is produced in the distillation of hydrate of ethyl-methyl-conine (p. 173), and passes over as a colourless oil, which is yellowish towards the end of the distillation.

It is a volatile, colourless oil smelling like conine. It is lighter than water. When burnt with oxide of copper, it yields 18.09 volumes of carbonic acid to 1 volume of nitrogen gas.

With iodide of ethyl it forms a crystalline product, in all probability ethyl-methyl-conine.

### Ethyl-conine.



V. PLANTA & KEKULÉ. (1854.) *Ann. Pharm.* 89, 131; *Pharm. Centr.* 1854, 278.

*Formation* (p. 164).

*Preparation.* Conine is placed together with iodide of ethyl in a sealed tube, and heated for half an hour to  $100^{\circ}$ , or until no further diminution of the iodide of ethyl takes place on continuing the application of heat; an upper stratum of viscid hydriodate of ethyl-conine is then formed, and a substratum of the excess of iodide of ethyl. The contents of the tube are dissolved in water, and the solution decanted off from the iodide of ethyl, the remainder of which is removed by a prolonged gentle heat. On adding potash, the ethyl-conine is precipitated as a reddish-yellow oil, which is rendered anhydrous by treating it with chloride of calcium and pieces of hydrate of potash frequently renewed. (Thus prepared it still contains a little water.)

If the conine contains methyl-conine, which is generally the case with commercial conine, iodide of ethyl forms crystalline hydriodate of ethyl-methyl-conine as well as oily hydriodate of ethyl-conine. The former is not decomposed by potash: hence, if the contents of the tube are mixed with potash and allowed to stand quietly, it separates out in crystals, while the brown oily ethyl-conine floats on the surface of the liquid. The ethyl-conine separated by the potash contains, moreover, another base, less rich in carbon; and if the ethyl-conine is

again submitted to the action of iodide of ethyl, this base forms a product of the same composition as the hydriodate of ethyl-methyl-conine; it is therefore probably formed from a base,  $C^{14}NH^{13}$ , originally contained in the conine:



It is only by treating the mixture with iodide of ethyl, that the resulting products can be separated by the method given for biethyl-conine.

*Properties.* Ethyl-conine is a volatile and almost colourless oil which refracts light strongly and is lighter than water. It does not exhibit a constant boiling point when distilled; the product which passes over last has a lower specific gravity, probably because it contains water. It smells very much like conine.

v. Planta & Kekulé.											
				a.			b.			c.	d.
20 C .....	120	....	78.43	.....	74.87	....	74.74	....	75.17	....	78.23
N .....	14	....	9.15	.....	8.74	....	8.74	....	8.65	....	9.08
19 H .....	19	....	12.42	.....	12.29	....	12.39	....	12.83	....	12.69
<hr/>											
C <sup>20</sup> NH <sup>19</sup> .....	153	....	100.00	.....	95.90	....	95.87	....	96.65	....	100.00

v. Planta & Kekulé ascribe the loss in their analyses *a*, *b*, and *c*, to oxygen, owing to the ethyl-conine which they analysed, containing water; they obtain the numbers represented under *d*, after deducting an amount of water equivalent to this oxygen, and calculating the remainder to 100.

Ethyl-conine is converted by iodide of ethyl in the cold, and completely after standing for 12 hours, into hydriodate of biethyl-conine, which solidifies into a crystalline mass.

*Combinations.* Ethyl-conine is but very slightly soluble in water; the cold-saturated solution becomes turbid when heated.

Ethyl-conine possesses basic properties. It dissolves readily in acids and develops much heat. Its salts do not crystallise on evaporation.

*Hydriodate of Ethyl-conine.* — (For preparation see page 170.) — It does not become crystalline by standing for a long time in vacuo over sulphuric acid. With freshly precipitated oxide of silver, it forms iodide of silver, while ethyl-conine is separated.

*Hydrochlorate of Ethyl-conine.* — Dried conine placed in vacuo beside a vessel containing strong hydrochloric acid, forms white vapours and then yields a mass of crystals which deliquesce rapidly on exposure to the air.

*Chloromercurate of Ethyl-conine.* — Corrosive sublimate forms with hydrochlorate of ethyl-conine, a white precipitate which agglomerates in resinous masses. It melts when heated, and separates from its hot solution on cooling in oily drops which become solid and crystalline; from its dilute solution, it is deposited in rhombic tables approaching very nearly to the square form.

*Chloraurate of Ethyl-conine.* — Trichloride of gold causes a yellow turbidity with hydrochlorate of ethyl-conine, and then precipitates a reddish yellow oil which solidifies and crystallises. From a hot dilute solution it may be obtained in beautiful yellow crystals.

*Chloroplatinate of Ethyl-conine.* — When the alcoholic solution is evaporated over sulphuric acid, the salt is obtained as a yellow crystalline powder, or in smaller quantity by precipitating the solution with ether. The precipitate is washed with ether-alcohol. It is readily soluble in water and in alcohol.

					v. Planta & Kekulé.
20 C	.....	120	....	38.41	..... 33.16
N	.....	14	....	3.90	
20 H	.....	20	....	5.57	..... 5.83
Pt	.....	99	....	27.47	..... 27.67
3 Cl	.....	106.2	....	29.65	
<hr/> C <sup>20</sup> NH <sup>19</sup> , HCl, PtCl <sup>3</sup> .....					359.2 .... 100.00

### Biethyl-conine.



V. PLANTA & KEKULÉ. *Ann. Pharm.* 89, 146.

*Diethyl-conine.* Known only in combination with water and acids.

*Preparation.* When ethyl-conine and iodide of ethyl are mixed together, and the vessel is placed in boiling water, the crystals of hydriodate of biethyl-conine which were at first formed, melt and solidify again on cooling. They contain (besides an excess of iodide of ethyl), a little hydriodate of ethyl-methyl-conine (or an isomeric compound), which for the most part remains undissolved after prolonged washing with alcohol.

On treating the aqueous solution of the hydriodate of biethyl-conine with freshly precipitated oxide of silver, aqueous biethyl-conine is obtained; it has a strong alkaline reaction, is inodorous, and tastes bitter.

*Hydriodate of Biethyl-conine.* — (For preparation see above.) — Crystals similar to those of hydriodate of ethyl-methyl-conine, but smaller, softer and less sharply defined. It dissolves readily in water and in alcohol, less readily in ether.

Hydrochlorate of biethyl-conine forms with *corrosive sublimate* a white flocculent precipitate which melts when heated, and is deposited in the crystalline state if the hot solution is allowed to stand for a long time.

*Chloraurate of Biethyl-conine.* — Sulphur-yellow, semifluid precipitate. Dissolves when heated and separates on cooling in oily drops which become solid and crystalline.



**Chloroplatinate of Biethyl-conine.** — Hydrochlorate of biethyl-conine does not precipitate a solution of bichloride of platinum, but on evaporating the mixed solutions on a water-bath, a crystalline salt is deposited, which is washed with alcohol. (If the biethyl-conine contains ethyl-methyl-conine, chloroplatinate of ethyl-methyl-conine is precipitated from concentrated solutions.)

					v. Planta & Kekulé.
24 C	.....	144	...	37.19	..... 36.93
N	.....	14	...	3.61	
24 H	.....	24	...	6.20	..... 6.66
Pt	.....	99	...	25.49	..... 25.56
3 Cl	.....	106.5	...	27.51	
<hr/>					
$C^{24}NH^{23}, HCl, PtCl^3$ .....					387.5 ... 100.00

### Ethyl-methyl-conine.



V. PLANTA & KÉKULÉ. *Ann. Pharm.* 89, 135.

If 1 H is supposed to be added to ethyl-methyl-conine, it becomes ethyl-methyl-conine-ammonium.

Known only as hydrate and in combination with acids.

It is obtained in aqueous solution by decomposing the hydriodate of ethyl-methyl-conine (p. 172) with freshly precipitated oxide of silver. The solution is colourless and inodorous; tastes strongly bitter, reacts alkaline, and in the concentrated state dissolves the epidermis like caustic potash. On evaporating the solution, it absorbs carbonic acid and leaves a colourless, partly crystalline (from containing carbonate), deliquescent mass, which, when distilled in water, decomposes into olefant gas and methyl-conine, leaving traces of carbon.

When a concentrated solution of ethyl-methyl-conine is heated with iodide of ethyl, the hydrate is converted into hydriodate of ethyl-methyl-conine, alcohol being formed at the same time.

**Combinations.** Ethyl-methyl-conine combines with hydrochloric, sulphuric, nitric, oxalic and acetic acids, forming crystallisable salts which are deliquescent and very soluble in water.

**Carbonate of Ethyl-methyl-conine.** — Aqueous ethyl-methyl-conine absorbs carbonic acid from the air; and on evaporating the solution in an atmosphere of carbonic acid, long needles of the carbonate are obtained.

**Hydriodate of Ethyl-methyl-conine.** — Formed: 1. by heating methyl-conine (also that which is contained in commercial conine) with iodide of ethyl. — 2. By heating ethyl-methyl-conine with an alkaline solution of iodide of potassium, crystals of hydriodate of ethyl-methyl-conine then separating out. — 3. By heating hydrate of ethyl-methyl-conine with iodide of ethyl (p. 172).



**Preparation.** 1. The product, obtained as described at p. 170, by treating commercial conine containing methyl-conine, with iodide of ethyl, is dissolved in water and mixed with potash. A brown oil at first separates out, and then two strata are formed, the lower of which solidifies into crystalline hydriodate of ethyl-methyl-conine; more of this latter product separates out in crystals from the potash-liquor on standing. The oil (ethyl-conine) which floats on the surface of the liquid, and the potash, are poured off from the crystals, which are then shaken with ether-alcohol (pure ether causes them to adhere together), and washed with ether-alcohol on a funnel plugged with asbestos until all the potash is removed. — 2. The product of the action of iodide of ethyl on commercial conine is washed with ether-alcohol, which takes up the hydriodate of ethyl-conine and the excess of iodide of ethyl.

**Properties.** Hydriodate of ethyl-methyl-conine, obtained by precipitation, forms a snow-white crystalline powder; from water, alcohol or potash, it crystallises in beautiful needles. It does not lose weight when dried at 100° in vacuo over sulphuric acid.

					v. Planta & Kekulé.	
22 C	.....	132	...	44.89	.....	44.87
N	.....	14	...	4.76		
22 H	.....	22	...	7.48	.....	8.36
I	.....	126	...	42.87	.....	42.98
<hr/>						
C <sup>22</sup> NH <sup>21</sup> ,HI	.....	294	...	100.00		

It melts when heated, at first without undergoing decomposition, and solidifies into a crystalline mass on cooling. If more strongly heated, it decomposes into iodide of ethyl and a base smelling like conine, which distil over and quickly recombine; this occurs partially even during the distillation.

Hydriodate of ethyl-methyl-conine dissolves in water, especially in warm water. It does not dissolve in alkaline liquids. It is precipitated by cold potash from its aqueous solution, but is dissolved by hot potash and crystallises out again on cooling.

It is soluble in alcohol, but to a less extent than hydriodate of biethyl-conine. It is insoluble in ether.

**Chloromercurate of Ethyl-methyl-conine.** — *a*. With 5 atoms of chloride of mercury. The compound *b* heated with water melts, dissolves, and after standing for some time deposits *a* in large crystals.

					v. Planta & Kekulé.	
22 C	.....	132	...	14.98	.....	14.25
N	.....	14	...	1.59		
22 H	.....	22	...	2.50	.....	2.70
6 Hg	.....	500	...	56.75	.....	55.78
6 Cl	.....	213	...	24.18		
<hr/>						
C <sup>22</sup> NH <sup>21</sup> ,HCl,5HgCl	.....	881	...	100.00		

*b*. With 6 atoms of chloride of mercury. Obtained, by pouring aqueous hydrochlorate of ethyl-methyl-conine into a solution of corrosive sublimate, as a white, distinctly crystalline precipitate. It dissolves rather easily in water, alcohol and in ether.

					v. Planta & Kekulé.	
22 C	.....	132	...	12.98		
N	.....	14	...	1.38		
22 H	.....	22	...	2.16		
6 Hg	.....	600	...	59.03	.....	59.15
7 Cl	.....	248.5	...	24.45	.....	24.53
<hr/>						
$C^{22}NH^{21}, HCl, 6HgCl$					1016.5	100.00

*Chloraurate of Ethyl-methyl-conine.* — Terchloride of gold precipitates from aqueous hydrochlorate of ethyl-methyl-conine, a sulphur-yellow, flocculent precipitate which rapidly becomes crystalline. From its hot aqueous solution, it is deposited in slender needles on cooling. When dried, it melts below  $100^{\circ}$ , and solidifies into a crystalline mass on cooling.

					v. Planta & Kekulé.	
$C^{22}NH^{21}Cl^4$	.....	810	...	61.14		
Au	.....	197	...	38.86	.....	38.67
<hr/>						
$C^{22}NH^{21}, HCl, AuCl^3$					507	100.00

*Chloroplatinate of Ethyl-methyl-conine* is sometimes precipitated as a yellow crystalline salt on mixing together the aqueous solutions of hydrochlorate of ethyl-methyl-conine and bichloride of platinum; if, however, the solutions are more dilute, it is deposited after a time in beautiful octohedrons which are slightly soluble in cold water and more soluble in hot water, but insoluble in alcohol and in ether.

					v. Planta & Kekulé.	
22 C	.....	132	...	35.37	.....	35.49
N	.....	14	...	3.75		
22 H	.....	22	...	5.89	.....	6.54
Pt	.....	98.7	...	26.45	.....	26.43
3 Cl	.....	106.5	...	28.54		
<hr/>						
$C^{22}NH^{21}, HCl, PtCl^2$					373.2	100.00

*Primary Nucleus*  $C^{16}H^{16}$ .

*Oil of Wine.*  $C^{16}H^{16}$ .

SERULLAS. *Ann. Chim. Phys.* 39, 153.

MARCHAND. *J. pr. Chem.* 15, 10.

*Light or sweet oil of wine* consists partly of this compound, *Oleum vini*, *Huile douce du vin*, *Etherol*, *Weinöl*.

*Formation and Preparation.* When sulphovinate of wine-oil is decomposed by water or aqueous alkalis, an oily body is formed, which floats on the surface of the liquid; if this oil is collected and left to itself, in a cool place, for several days, it deposits crystals of etherin. The oil containing the crystals, is washed on a moistened filter, with water, as long as the wash-water continues to exhibit an acid reaction; the funnel is then placed over a bottle; and after the filter has become dry, the oil of wine runs through and the etherin remains on the filter. (The filter remains

saturated with oil of wine, which may be extracted by ether-alcohol, and remains behind when the ether-alcohol is evaporated.) (Serullas.) — Marchand dries oil of wine thus obtained in vacuo.

*Properties.* Yellowish oil having a peculiar aromatic odour. Sp. gr. = 0.921. Boils at  $280^{\circ}$ . When submitted to cold, it becomes less fluid; at  $25^{\circ}$  it is viscid like turpentine; at  $35^{\circ}$  it is solid. In the anhydrous state it does not conduct electricity. (Serullas.)

				Serullas. ;		Marchand.
						mean.
16 C .....	96	....	85.71	.....	83.4 to 86.0	.... 84.38
16 H .....	16	....	14.29	.....	13.3 to 13.9	.... 14.15
$C^{16}H^{16}$ .....	112	....	100.00	.....	96.7 99.9	.... 98.53

Oil of wine mixes with *anhydrous sulphuric acid*, evolves heat, turns brown, and gives off an ethereal odour, while the sulphuric acid deliquesces. If the mixture is made carefully, no sulphurous acid is evolved; and, on saturating the mixture with baryta, a soluble baryta-salt is obtained, which burns on platinum foil with a brilliant flame, leaving a residue of strongly tumefied charcoal and sulphate of baryta, and, when melted with potash, yields sulphurous acid and an inflammable gas; the salt cannot be obtained crystallised, and therefore probably consists of ethionate of baryta. (Marchand.)

Oil of wine dissolves, without alteration, in oil of vitriol, and is precipitated from the solution by water; if, however, it is warmed, an acid is formed, which yields a soluble salt with baryta. (Marchand.)

### Etherin.

HENNEL. *J. of Sc.* 19, 96; *Phil. Trans.* 1826, 240; *Schw.* 49, 58; *Pogg.* 9, 12.

SERULLAS. *Ann. Chim. Phys.* 39, 153

MARCHAND. *J. pr. Chem.* 15, 10.

*Weinölcamphor, Camphor or Stearoptene of wine-oil.*

*Formation.* By boiling sulphovinate of wine-oil with caustic-potash (Hennel). It is deposited in the cold from the light oil of wine obtained by decomposing sulphovinate of wine-oil with water or aqueous alkalis. (Marchand, Serullas). Formed also from sulphovinate of wine-oil, which has become thick by keeping. (Hennel.)

*Preparation* (p. 175). The etherin which remains on the filter after the oil of wine has run off, is distilled in a bent glass tube, and the solidified distillate is melted and poured out in thin layers, which are repeatedly pressed between blotting paper, as long as the paper continues to take up oil. (Serullas.)

**Properties.** Etherin forms long brilliant, transparent prisms (Serullas), resembling naphthalin. (Hennel.) It is tasteless, but has a peculiar aromatic odour, like that of wine-oil, especially when heated. It is friable and grates between the teeth. Sp. gr. = 0.98. (Serullas.) Melts a little above 100° (Hennel), at 110° (Serullas), into a clear liquid. Distils at 260°, without leaving a residue. (Serullas.)

				Hennel.	Marchand.
					<i>mean.</i>
16 C .....	96	...	85.71	82.11	84.60
16 H.....	16	...	14.29	13.44	14.30
<hr/>					
C <sup>16</sup> H <sup>16</sup> .....	112	...	100.00	95.55	98.90

Isomeric with oil of wine. (Serullas.) Fechner supposed etherin to contain oxygen. (*Schw.* 49, 73.)

**Decompositions.** 1. Etherin is decomposed, at a red heat, into charcoal and a hydrocarbon. (Serullas.) With anhydrous *sulphuric acid* and with *oil of vitriol* it behaves like oil of wine (p. 176). (Marchand.) Dissolves in warm sulphuric acid with pale-red colour; in cold *nitric acid*, with dark-red colour, which is destroyed by heat, after which a white precipitate is produced on the addition of water. (Hennel.)

Etherin is insoluble in water (Serullas), also in hydrochloric acid, aqueous alkalis, and acetic acid, even when heated. (Hennel.) It dissolves in alcohol and in ether, and crystallises from the solutions in prisms. (Hennel, Serullas.)

### *Appendix to Oil of Wine.*

#### The so-called Sulphovinate of Wine-oil.



HENNEL. *J. of Sc.* 19, 96; *Phil. Trans.* 1826, 240; *Schw.* 49, 58; *Pogg.*

9, 12; *Phil. Trans.* 1828, 365; *Pogg.* 14, 273; abstr. *Schw.* 55, 116.

SERULLAS. *Ann. Chim. Phys.* 39, 153; *Pogg.* 15, 20.

LIEBIG. *Pogg.* 21, 40.

ZEISE. *Pogg.* 31, 371.

MARCHAND. *J. pr. Chem.* 15, 8.

**Oil of wine.** (Hennel, Marchand.) *Double sulphate of ether and carburetted hydrogen; neutral sulphate of carburetted hydrogen* (Serullas); *ethyl-sulphate of etherol; æthylschwefelsaures Aetherol* (Liebig); *sulphate of ethyl and etherol, schwefelsaures Aethyloxyd-Aetherol* (Berzelius); *sulphate of etherin*. Discovered by Hennel, in 1826.

**Formation.** Passes over in the preparation of ether, towards the end of the distillation (viii, 237). It is formed, but in exceedingly small quantities, not only on distilling, but immediately on mixing alcohol with sulphuric acid. (Marchand.) It is also produced when ether is acted upon by anhydrous sulphuric acid in the preparation of isethionic

acid (Liebig, viii, 429), and by the dry distillation of the sulphovicates (viii, 417.)

**Preparation.** 1. When 1 part of alcohol is distilled with  $2\frac{1}{2}$  parts of sulphuric acid, a little ether passes over first, then a yellowish oil and an aqueous ethereal liquid; the former is separated from the latter, and freed from uncombined sulphuric acid and a part of the sulphurous acid, the alcohol, and the ether, by agitation with water (which, according to Liebig, should be ice-cold). The oil is then separated from the water and placed over sulphuric acid under the receiver of an air-pump, which is slowly exhausted in order that the evaporation of the ether and sulphurous acid may not cause the liquid to boil violently. (Serullas.) Liebig finally treats it with fused chloride of calcium. — 2. Crystallised sulphovinate of lime is dried carefully but completely in vacuo, and submitted to dry distillation. The distillate is purified as in the first method. (Serullas.) Liebig mixes with the sulphovinate of lime, which is dried completely and with the greatest care, an equal weight of freshly burned lime, and distils the mixture at a moderately high temperature. The distillate, which contains the sulphovinate of wine-oil dissolved in alcohol, is mixed with water, which precipitates the oil, and dried over sulphuric acid in vacuo. Marchand obtained less oil of wine on adding lime than without it; he therefore recommends the distillation *per se* of the sulphovicates, especially of the basic lead-salt. Hennel washed the sulphovinate of wine-oil, which passes over towards the end of the distillation in the preparation of ether, with carbonate of potash and water, and removed the ether by evaporation. — But the carbonate of potash removes sulphovinic acid. (Hennel; Liebig, *Handwörterbuch*, i, 122.)

**Properties.** Yellow oil, thicker than volatile oils. (Hennel.) When moist it is colourless and transparent. After remaining for 24 hours under the receiver of an air-pump, it acquires a dark-green colour, but becomes colourless again on being shaken up with water or exposed for a long time to the air; the oil rendered colourless by water, remains so even in contact with potassium, but becomes green again when heated. (Serullas.) — Liebig and Marchand were never able to obtain sulphovinate of wine-oil coloured green; Marchand is, therefore, of opinion that the coloration observed by Serullas, arose from some accidental impurities. Sp. gr. = 1.05 (Hennel); 1.133 (Serullas). It has a peculiar, penetrating, aromatic odour, and a sharp, fresh, somewhat bitter taste; rather like that of mint. (Serullas.) It is neutral. (Liebig.)

					Serullas.		Liebig.		Marchand.
8 C .....	48	...	33·10	.....	33·05	...	32·76	...	33·13
9 H .....	9	...	6·21	.....	6·19	...	6·04	...	6·23
O .....	8	...	5·52	.....	5·58	} ...	61·20	...	{ 5·95
2 SO <sup>3</sup> .....	80	...	55·17	....	55·02				
<hr/>									
C <sup>8</sup> H <sup>8</sup> S <sup>2</sup> O <sup>7</sup> ...	145	...	100·00	.....	99·84	...	100·00	...	100·00

Hennel found 53.7 C, 8.3 H, and 38 SO<sup>3</sup>.

**Decompositions.** 1. The oil becomes thicker after a few months and deposits crystals of etherin. (Hennel.) When pure and kept in sealed tubes it undergoes no change. (Serullas.) — 2. When it is distilled, the greater part passes over undecomposed, and yields a distillate which has

the same composition from first to last (Marchand); towards the end, however, it evolves a quantity of sulphurous acid, and leaves sulphuric acid and charcoal. (Hennel.)—3. When placed under *water*, it decomposes, after some time, into crude oil of wine (a mixture of oil of wine and etherin), which ascends to the surface, and aqueous sulphovinic acid. If but little water is used, this decomposition takes place very slowly; if the oil is warmed with water, it takes place in a few seconds. (Serullas, Marchand.)—4. When treated with aqueous *alkalis*, it immediately decomposes into a salt of sulphovinic acid and crude oil of wine. (Serullas.) Sulphovinate of wine-oil treated with caustic potash decreases visibly in bulk and becomes more viscid. If the undissolved portion is purified from potash by ether, there remains, after evaporation of the ether, a yellow and very thick oil, which volatilises completely when heated, without undergoing decomposition. This oil, if allowed to stand for several days, solidifies into a crystalline mass of etherin. (Hennel.) When sulphovinate of wine-oil is heated with aqueous potash, it becomes turbid, then white and untransparent, but no lighter oil rises to the surface. After the alkaline liquid has been removed by washing with water, water poured upon the oil becomes acid. If the oil be now distilled in a retort with a large quantity of water, it disappears as the boiling continues, and yields a distillate having a slightly ethereal odour, with a small quantity of transparent colourless oil floating on its surface; this oil solidifies, completely, into a crystalline mass at 0°. (Liebig.)—5. *Potassium* does not decompose sulphovinate of wine-oil in the cold; but, on heating, olefiant gas, with a smell of garlic, is evolved, and there remains a residue of charcoal mixed with a little sulphide of potassium and a large quantity of sulphate of potash. (Serullas.)—6. With a concentrated solution of tersulphide or pentasulphide of potassium in alcohol, it forms, in a few minutes, a neutral liquid, from which a large quantity of sulphovinate of potash is soon deposited, and also sulphur, if pentasulphide of potassium is used. The liquid which is poured off is alcohol, containing in solution an oil rich in sulphur, either thialol or a mixture of this oil with oil of wine which has been acted upon by sulphuretted hydrogen. This sulphuretted oil is yellowish, heavier than water, and has a most repulsive alliaceous odour; it can scarcely be distilled by itself, and passes over very slowly when distilled with water. Its alcoholic solution does not precipitate a solution of acetate of lead; if hydrate of potash dissolved in almost absolute alcohol is added to it, a clear mixture is formed, which does not change; if, however, the alcohol contains more water, a considerable quantity of hyposulphite of potash is deposited in 48 hours. This oil is also formed when sulphovinate of wine-oil is shaken up with *aqueous* pentasulphide of potassium, and collects, for the most part, at the bottom of the aqueous solution of the sulphovinate of potash. If too little sulphovinate of wine-oil was used, the filtrate yields, when heated, a fresh quantity of oil, which appears to be the same as the first, and the sulphovinate of potash is converted into sulphate. (Zeise.)

Sulphovinate of wine-oil is slightly soluble in water. (Serullas.) It dissolves readily in alcohol and in ether (Hennel), from which it may be precipitated by water. (Serullas.)

Caprylene  $C^{16}H^{16}$ .CAHOURS. *Compt. rend.* 31, 143.J. BOUIS. *Compt. rend.* 33, 144; 38, 936; *Ann. Pharm.* 92, 396;  
*N. Ann. Chim. Phys.* 44, 114.M. BERTHELOT. *Compt. rend.* 44, 1350; *Ann. Pharm.* 104, 185.

Octylene (Gerhardt); Pryle (Gm.).

**Formation.** Caprylene is formed, together with gaseous hydrocarbons, marsh-gas, and hydrogen, when pelargonic acid is distilled with potash-lime. (Cahours.)—2. By heating caprylic alcohol with sulphuric acid or with chloride of zinc. (Caprylic alcohol and sulphuric acid, mixed in the cold, form caprylene, together with sulphocaprylic acid and sulphate of capryl).—3. By heating iodide or chloride of capryl with sodium or mercury. (Bouis.)

**Preparation.** 1. An intimate mixture of 1 part of pelargonic acid with 4 parts of potash-lime is heated nearly to dull redness, and the clear mobile amber-yellow distillate is rectified, the temperature then rising from  $105^{\circ}$  to  $140^{\circ}$ . The greater part, consisting of caprylene, passes over between  $106^{\circ}$  and  $110^{\circ}$ . (Cahours.)—2. When caprylic alcohol is distilled with sulphuric acid, the mixture blackens and evolves sulphurous acid, while caprylene distils over as a colourless oil, which is purified by washing with water and rectifying *per se*. (Bouis.)—3. Fused chloride of zinc dissolves readily in caprylic alcohol; on heating the liquid, water undecomposed caprylic alcohol and caprylene pass over, and the caprylene is obtained pure by removing the water and pouring back the distillate two or three times. (Pure caprylic alcohol is completely converted into caprylene by a single distillation with fused chloride of zinc, the temperature remaining stationary at  $125^{\circ}$ . (Bouis.)

**Properties.** Colourless, strongly refracting liquid, having a somewhat powerful odour. Boils at  $125^{\circ}$  (Bouis); if prepared by the first method, between  $106^{\circ}$  and  $110^{\circ}$ . (Cahours.) Specific gravity = 0.723 at  $17^{\circ}$  (Bouis); when prepared according to 1, its sp. gr. is 0.708 at  $16^{\circ}$ . (Cahours.) Vapour-density of caprylene prepared according to 1, = 3.954; according to 2, = 3.90.

				Cahours.				Bouis.			



*Decompositions.* 1. Caprylene burns with a very bright flame.— 2. Heated with *bromine* it forms a heavy liquid,  $C^{16}H^{16}Br^2$ . (Cahours.) Bromine dropped into caprylene produces a hissing sound and forms a thick, colourless liquid. (Bouis.)— 3. Caprylene acted upon by *chlorine* becomes so violently heated that it takes fire. If the action is allowed to proceed more slowly, and finally terminated in sunshine, hydrochloric acid is evolved and pentachloride of caprylene is formed. (Bouis.)— 4. One volume of caprylene rapidly absorbs, at ordinary temperatures, from 7 to 8 volumes of *hydrochloric acid gas*, and then slowly takes up more, so that in two hours, 10 volumes are absorbed; in 5 days, 12 volumes; in 11 days, 13 volumes; in 17 days, 14 volumes; and in 23 days, 15 volumes; chloride of capryl is formed, which, after it has been shaken with aqueous potash, may be separated by distillation. If caprylene is heated with a saturated aqueous solution of hydrochloric acid at  $100^\circ$ , chloride of capryl is formed, but the transformation is not complete, even after heating for 100 hours. (Berthelot.)— 5. Caprylene is violently attacked by concentrated nitric acid, and forms nitro- and binitro-caprylene. (Bouis.) When concentrated nitric acid is dropped upon caprylene, a violent action takes place, and the mixture begins to boil, with evolution of nitrous acid. On cooling, the liquid separates into two strata, the upper, which is yellow and oily, consisting of nitro- and binitro-caprylene, and the lower of nitric acid. From the latter, white prismatic crystals are often deposited, consisting of an acid which is readily soluble in alcohol. This acid is more certain to be obtained when the nitric acid is added in small portions at a time, and the resulting action is allowed to subside before any fresh acid is added. It melts when heated, and evolves thick white irritating vapours; with potash and oxide of silver, it forms salts, the latter of which explodes when heated and dissolves in ammonia and nitric acid, but not in water. (Bouis.)— 6. With fuming nitric acid, caprylene forms binitrocaprylene. (Bouis.)— 7. When an alcoholic solution of caprylene is treated, first with nitric acid, then with ammonia, and lastly with sulphuretted hydrogen, sulphur is deposited, and thin yellow needles are formed, which become white on exposure to the air, and when heated, melt, swell-up, and burn with a white flame, leaving a residue of charcoal. Perhaps the body is  $C^{16}NH^{17}$ . (Bouis.)— 8. Caprylene heated with *sodium* is not attacked; but, if dry chlorine gas is passed into the liquid, the compound  $C^{16}H^{15}ClNa^2$  is immediately formed with evolution of hydrogen:



With iodine or bromine, the corresponding iodine and bromine compounds are formed. (Bouis.)

*Combinations.* Caprylene is insoluble in water. It dissolves iodine in large quantities and becomes red. (Caprylene removes iodine from its aqueous solution.) It dissolves iodide of mercury, when heated with it. (Bouis.) Caprylene is readily soluble in alcohol and in ether.



**Metacaprylene.**BOUIS. *N. Ann. Chim. Phys.* 44, 124.

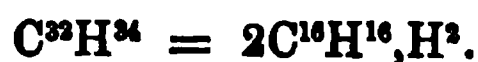
When Nordhausen sulphuric acid is allowed to act upon caprylic alcohol for a long time, there collects on the surface of the liquid a transparent layer of oil, which gradually increases in quantity. The oil, which is metacaprylene, is obtained pure by washing it with water, alcohol, and aqueous potash.

It is inodorous and colourless. Begins to boil at  $250^{\circ}$ , the temperature then rising and the liquid acquiring an unpleasant odour of perspiration. Sp. gr. = 0.814 at  $15^{\circ}$ .

					Bouis.
16 C .....	96	...	85.71	.....	85.74
16 H .....	16	...	14.29	.....	13.93
<hr/>					
$C^{16}H^{16}$ .....	112	...	100.00	.....	99.67

Isomeric with caprylene.

Burns with a smoky flame. Is not acted upon by boiling potash. Insoluble in water and scarcely soluble in cold alcohol.

**Capryl.**BOUIS. *N. Ann. Chim. Phys.* 44, 143.

*Octyl.* (Gerhardt.)

*Preparation.* Potassium or sodium in contact with cold chloride of capryl immediately becomes covered with a white crust, which separates from the metal on agitation, and is continually renewed. The pasty mass is pressed out, and fresh sodium added to the liquid, till it has been deprived of all its chlorine and no longer acts upon sodium on boiling.

Capryl is fluid and lighter than water. It burns with a brilliant flame.

					Bouis.
32 C .....	192	...	84.95	.....	84.98
34 H .....	34	...	15.05	.....	14.91
<hr/>					
$C^{32}H^{34}$ .....	226	...	100.00	.....	99.89

Perhaps a mixture of  $C^{16}H^{16}$  and  $C^{16}H^{16}$  (Bouis).

## Caprylic Ether?



BOUIS. *N. Ann. Chim. Phys.* 44, 138.

Bouis obtained, by distilling sodium-capryl alcohol with chloride of capryl, a liquid of peculiar odour, which passed over at  $50^{\circ}$ , and afterwards at an increasing temperature. It contained 75.97 C and 13.05 H ( $\text{C}^{16}\text{H}^{17}\text{O} = 79.3 \text{ C and } 14.0 \text{ H}$ ), and must have contained traces of chloride of capryl. The same liquid was obtained by following the method employed by Balard (xi, 7) in the preparation of amylic ether.

## Caprylic Alcohol.



- J. BOUIS. (1851.) *Compt. rend.* 33, 144; *Ann. Pharm.* 80, 304; *Institut.* 1851, 258; *Ann. Pharm.* 80, 306; *Compt. rend.* 38, 935; 39, 288; *Ann. Pharm.* 92, 395; *N. Ann. Chim. Phys.* 44, 103; *Compt. rend.* 41, 603; *N. Ann. Chim. Phys.* 48, 99; *Ann. Pharm.* 97, 34.
- W. L. MOSCHNIN. *Ann. Pharm.* 87, 111; *Pharm. Centralbl.* 1854, 171.
- R. RAILTON. *Chem. Soc. Qu. J.* 6, 205; *Pharm. Centr.* 54, 256.
- WILLS. *Chem. Soc. Qu. J.* 6, 307; *N. Ann. Chim. Phys.* 41, 103.
- W. S. SQUIRE. *Chem. Soc. Qu. J.* 7, 108; *Pharm. Centr.* 1855, 256; *Ann. Pharm.* 92, 400.
- FAGET. *Compt. rend.* 37, 780; *Ann. Pharm.* 88, 325.
- CAHOURS. *Compt. rend.* 39, 254; *Ann. Pharm.* 92, 399.
- LIMPRICHT. *Ann. Pharm.* 93, 242; *N. Ann. Chim. Phys.* 43, 490; *Epistolary Communication.*
- STÄDELER. *J. pr. Chem.* 72, 241.

## Octylic alcohol, Hydrate of Octyl.

The oil which Bouis obtained by the method described on the following page was first regarded by him as caprylic alcohol, then as œnanthyl alcohol; but ultimately he returned to his first opinion, which was afterwards corroborated by Moschnin, Squire and Cahours. Railton and Wills, on the contrary, consider it to be œnanthyl alcohol, while Limpricht regards it as caprylic aldehyde. According to Städeler, œnanthol is formed in the simple distillation of ricinolate of soda, and if an excess of hydrate of soda is employed, the products are œnanthyl alcohol and methylœnanthal.

*Formation.* By the action of hydrate of potash upon castor-oil, ricinolamide or ricinolic acid. (Bouis.) — 2. When fusel-oil prepared from the marc of grapes, is distilled, the less volatile portion which passes over between  $160^{\circ}$  and  $165^{\circ}$  is found to consist of a mixture of œnanthyl alcohol and caprylic alcohol. (Faget.)

*Preparation.* Castor-oil is saponified with hydrate of potash or soda, and as much more alkali is added as amounts to half the oil employed. The whole is then heated moderately in an alembic, till the mass, which foams at first, has become thicker and the foam has subsided; it is then more strongly heated, so as to melt the alkali, as long as caprylic alcohol continues to distil over as a colourless, oily liquid. When stinking vapours begin to escape, the operation is stopped. In this reaction, hydrogen is evolved and sebate of potash remains in the residue :



If the heat is not strong enough to melt the alkali, caprylic aldehyde is formed. — As the mass is apt to overflow and stop the condenser, in which it solidifies, the capital of the alembic and the condenser are connected by a wide tube, which can be broken if necessary; or the lateral opening of the alembic is closed with a cork. (Bouis.) Wills saponifies castor-oil with potash, separates the soap with common salt, and melts the solid mass with one-third of its weight of hydrate of potash, until aromatic vapours are evolved; he then distils the whole from a copper alembic, taking care to avoid decomposing the sebate of potash.

*Purification.* The caprylic alcohol thus obtained, which amounts to one-fourth of the volume or one-fifth of the weight of the castor-oil employed, is repeatedly distilled over fresh pieces of potash, until no more brown substance remains in the residue. (Bouis.)

There then remains with the potash a brown and very viscid mass. On distilling impure caprylic alcohol with potash, a violent reaction takes place, the mass swelling up, and a brown liquid being formed. When this liquid is separated from the potash by water, it forms a brown oil lighter than water, of a strong irritating odour, of sp. gr. 0·840, readily soluble in ether and less soluble in alcohol. It contains 81·38 per cent. C and 13·57 per cent. H. (Bouis.) The oil obtained by distilling castor-oil with hydrate of potash is always a mixture of caprylic aldehyde with caprylic alcohol: hence it always unites with the alkaline bisulphites, and forms a soapy mass. On account of the greasy nature of this compound, the separation of the aldehyde from the alcohol is but incompletely effected by means of alkaline bisulphites, whereas in Bouis' method by rectification over hydrate of potash, the aldehyde is destroyed. (Limpricht.)

*Properties.* Caprylic alcohol is a colourless, transparent, oily liquid of a strong aromatic odour. It makes grease-spots on paper. Boils at 180° (Bouis); at 179° (Moschnin, Wills); at 179° (Squire.) Sp. gr. = 0·823 at 17° (Bouis); 0·792 at 16·5°. (Wills.) Vapour density = 4·55 (Bouis); 4·019. (Railton.) It is without action upon polarised light. (Bouis.)

					Bouis.		Moschnin.		Wills.	
16 C	.....	96	...	73·84	.....	73·46	...	73·64	....	72·79
18 H	.....	18	...	13·84	.....	13·88	...	13·80	....	13·67
2 O	.....	16	...	12·32	.....	12·66	...	12·56	....	13·54
<hr/>										
C <sup>16</sup> H <sup>18</sup> O <sup>2</sup>	.....	130	...	100·00	.....	100·00	...	100·00	....	100·00

	Vol.	Density.
C-vapour .....	16 .....	6.6560
H-gas .....	18 .....	1.2474
O-gas .....	1 .....	1.1093
<hr/>		
Caprylic alcohol vapour ....	2 .....	9.0127
	1 .....	4.5063

*Decompositions.* Caprylic alcohol burns with a white brilliant flame. — 2. It does not appear to be changed by exposure to the air. (Bouis.) When oxygen is passed through boiling caprylic alcohol, a large quantity of caprylic acid is formed. (Railton.) (According to Railton, who considers the alcohol as cenanthylic alcohol, the acid thus formed is cenanthylic acid.) Oxygen does not act at the boiling heat upon pure caprylic alcohol free from aldehyde. (Bouis.)

3. *Nitric acid* oxidises caprylic alcohol, and forms various fatty acids, amongst others caprylic acid, according to the concentration of the acid and the duration of the action. The reaction is violent, and accompanied with evolution of red vapours; on boiling, the liquids mix and fatty acids distil over. In one experiment, an acid oil insoluble in water, was obtained, from which fatty acids (amongst others, cenanthylic acid) distilled over from 140° to 145°, and then as the temperature rapidly rose, neutral empyreumatic oils came over. — When nitric acid was allowed to act for a longer time, an acid liquid was formed, probably containing caproic and butyric acids. — Dilute nitric acid produces crystals the same as those which it forms from caprylene (p. 181), and a layer of oil which floats on the surface of the liquid. Aqueous potash extracts from this oil cenanthylic and caprylic acids. The undissolved portion of the oil, after having been washed and dried, burns when heated, becomes black and emits acid vapours, leaving a residue of charcoal. Concentrated potash acts violently upon the oil, eliminating ammonia on the application of heat. (Bouis.)

4. *Sulphuric acid* dissolves readily in caprylic alcohol, and if the mixture is not cooled, imparts to it a red colour gradually becoming darker, and forms sulphocaprylic acid. Generally, also, sulphate of capryl and caprylene are formed at the same time. If the mixture, after standing for 24 hours, is poured into a concentrated aqueous solution of carbonate of potash, effervescence takes place, and the mixture becomes warm; the liquid then separates into three strata, the lowest of which consists of sulphate of potash, and the middle stratum of an aqueous solution of sulphate and carbonate of potash; the upper yellow oily stratum diminishes in bulk when washed with water, which dissolves from it caprylate of potash. The undissolved oil is brown, soluble in water, insoluble in potash; when distilled, it blackens, giving off sulphurous acid and caprylene, and leaves a residue of charcoal not containing potash. (Bouis.)

5. Caprylic alcohol acted upon by *fuming sulphuric acid*, is first converted into sulphocaprylic acid, and then, if the action is continued, into metacaprylene (p. 182). (Bouis.)

6. Caprylic alcohol submitted to the action of *pentachloride of phosphorus* is decomposed, with violent evolution of heat, into chloride of capryl and oxychloride of phosphorus. (Bouis.) — 7. Caprylic alcohol absorbs *hydrochloric acid gas* and evolves heat; on heating the liquid to a temperature between 120° and 130°, chloride of capryl is formed. (Bouis.) — 8. Fused *chloride of zinc* dissolves in caprylic alcohol, and forms a clear solution which, when heated at 125°, gives off water and caprylene. (Bouis.) — 9. When caprylic alcohol is acted upon by *glacial phosphoric acid* for a long time, phosphocaprylic acid is formed, which gives soluble salts with lime, baryta, and oxide of lead. (Bouis.) — 10. Caprylic alcohol forms with phosphorus and bromine, bromide of capryl; with phosphorus and iodine, iodide of capryl. (Bouis, Wills, Squire.) On heating caprylic alcohol with phosphorus and iodine, the

liquid divides into two strata, the lower of which yields phosphoretted hydrogen and phosphoric acid, and therefore probably contains hypophosphorous acid. During the reaction, hydrocarbons are almost always formed, apparently owing to the action of phosphoric acid upon the caprylic alcohol. (Bouis.) — 11. When *potassium* is thrown into caprylic alcohol, hydrogen is evolved and a compound is formed which may be considered as caprylic alcohol in which one atom of hydrogen is replaced by one atom of metal. Water decomposes the compound into caprylic alcohol and aqueous potash. (Bouis, Wills.) (In proportion as the potassium-compound is formed, the liquid becomes pasty, and assumes a yellow, and finally a reddish brown colour.) — When sodium is introduced into caprylic alcohol, it becomes bright and remains so without being acted upon; on heating, a violent action takes place, and the white compound is formed which turns brown on exposure to the air. The sodium-compound does not melt; it dissolves more abundantly in cold than in hot caprylic alcohol. (Bouis.) — 12. Caprylic alcohol heated with *alkalis* above  $250^{\circ}$ , gives off hydrogen, a hydrocarbon, and an acid. (Bouis.) — 13. *Caustic lime* decomposes caprylic alcohol at a high temperature, forming hydrogen and gaseous hydrocarbons. — 14. Caprylic alcohol reduces dry oxide of silver (but not nitrate of silver) on heating, and forms a metallic mirror. (Bouis.)

*Combinations.* Caprylic alcohol is insoluble in water.

It dissolves phosphorus, sulphur, and iodine. (Bouis.)

It rapidly absorbs gaseous *hydrochloric acid* with evolution of heat; on heating the liquid, the gas is evolved and leaves the caprylic alcohol unchanged. (Bouis.)

Combines with *chloride of calcium*, forming very deliquescent prisms, which dissolve more abundantly in cold than in hot caprylic alcohol, and are decomposed by water. (Bouis.)

Dissolves fused *chloride of zinc* and forms a clear solution.

Dissolves in *wood-spirit*, *alcohol* and *ether*, and very readily in *acetic acid*.

Dissolves *fats*, *resins*, and soft *copal* with readiness. Hard copal swells up in it and finally dissolves. (Bouis.)

### Violet-coloured substance.



Bouis. *N. Ann. Chim. Phys.* 44, 144.

*Formation.* By the action of sodium on chloride of capryl (p. 181). — 2. By heating chloride of capryl with sodium in a sealed tube. — 3. When caprylene is heated with sodium, and the mixture is acted upon by dry chlorine, the violet body is formed, with evolution of hydrogen, a portion of the caprylene remaining unaltered even if an excess of sodium is used. — 4. Caprylene is mixed with a small quantity of chloride of capryl, or with caprylene which has been treated with chlorine, and the mixture is submitted to the action of sodium.

The compound may be dried in vacuo at  $130^{\circ}$ , without suffering decomposition; merely becoming somewhat lighter in colour.

If exposed to the air after being pressed between paper, it becomes white, forming

soda and chloride of sodium. It sometimes takes fire spontaneously, probably owing to adhering sodium.

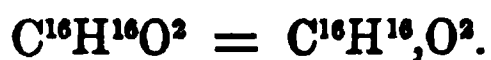
When heated, it evolves hydrogen, and leaves a residue of charcoal and finely divided sodium.

It is decomposed by nearly all liquids that contain oxygen. Placed in contact with water, it becomes exceedingly hot, and evolves a little hydrogen (probably owing to adhering sodium), and forms soda, chloride of sodium, and caprylene.

It is destroyed by chlorine, or by a large excess of chloride of capryl.

It may be preserved unaltered in rock-oil and in caprylene.

### Caprylic Aldehyde.



LIMPRICHT. *Ann. Pharm.* 93, 242; *N. Ann. Chim. Phys.* 43, 490; *Ann. Pharm.* 97, 370.

BOUIS. *Compt. rend.* 41, 603; *N. Ann. Chim. Phys.* 48, 99; *Ann. Pharm.* 97, 34.

STÄDELER. *J. pr. Chem.* 72, 241.

**Formation.** 1. By submitting castor-oil soap to dry distillation. (Bouis.) In this process only œnanthol distils over, which, when pure, boils between 151° and 152°, and there remains in the retort the soda-salt of the same acid as is formed when castor-oil is distilled alone. (Städeler.) — 2. By distilling castor-oil, or the soaps obtained from it, with potash. (Limpricht.) In this process, when an excess of potash is present, a mixture of caprylic alcohol and caprylic aldehyde is formed; the more gently the heat is applied, and the less the temperature exceeds 225° — 230°, the greater is the quantity of caprylic aldehyde obtained. (Bouis.) — 3. The distillate obtained from a mixture of caprylate and formiate of lime has the odour of caprylic aldehyde, and forms a crystalline compound with bisulphite of soda. (Limpricht.)

**Preparation.** 1. When the crude distillate obtained from castor-oil, as described at page 184, is shaken up with concentrated aqueous bisulphite of potash or soda, the liquid solidifies, in consequence of the formation of crystals, into a sticky mass, which is repeatedly pressed out between fresh folds of blotting paper, washed with alcohol, and dried over oil of vitriol. The product is afterwards dissolved in hot water, whereupon the caprylic aldehyde separates and may be dried over chloride of calcium and rectified. (Limpricht.) (See also p. 189.)

2. Castor-oil is saponified with soda, the soap precipitated by common salt and pressed, then dissolved in water and again precipitated by salt. The soap thus freed from excess of soda is washed, first with water containing salt and afterwards with pure water; it is then pressed, dried, and distilled in small portions, the mass swelling up and caprylic aldehyde passing over, which may be purified as in the first method. In this reaction, no gas is evolved, and the residue contains, not sebacic acid, but a new acid, perhaps  $\text{C}^{20}\text{H}^{18}\text{O}^4$ . (Bouis.)

3. Castor-oil soap obtained as above is decomposed with chloride

of barium, and the baryta-salt distilled at a gentle heat: the mass does not swell up. The distillate is purified as in the first method. (Bouis.)

*Properties.* Caprylic aldehyde is a colourless liquid (Limpricht), which refracts light strongly. (Bouis.) It has an aromatic odour (Limpricht); a strong odour recalling that of bananas. (Bouis). It has a caustic taste. Sp. gr. = 0.818 at  $19^{\circ}$  (Bouis); 0.820. (Limpricht.) Boils at  $178^{\circ}$  (Limpricht), at  $171^{\circ}$  under the common atmospheric pressure. (Bouis.)

					Limpricht.		Bouis.
16 C	.....	96	....	75.00	.....	74.49	.... 74.75
16 H	.....	16	....	12.50	.....	12.77	.... 12.66
2 O	.....	16	....	12.50	.....	12.74	.... 12.59
<hr/>							
$C^{16}H^{16}O^2$	.....	128	....	100.00	.....	100.00	.... 100.00

*Decompositions.* 1. Caprylic aldehyde burns with a brilliant and not smoky flame. (Bouis.) — 2. It becomes acid on exposure to the air. (Limpricht.) Air or oxygen does not appear to alter caprylic aldehyde in the cold; if however the liquid is warmed and air passed through, it rapidly becomes coloured and acid, but it is not always possible to convert the whole of the aldehyde into caprylic acid. Pure oxygen completely oxidises heated caprylic aldehyde, and acts so violently that an explosion may take place. (Bouis.) — 3. *Nitric acid* acts very violently upon caprylic aldehyde, and forms the same products as with caprylic alcohol. (Bouis.) — 4. When distilled with aqueous *chromate of potash* and *sulphuric acid*, it is partly converted into an acid, but the greater part remains unaltered. (Limpricht.) Heated with solid *hydrate of potash*, it is coloured brown, and forms a spongy mass which cannot be distilled; water separates from the latter a brown oil which behaves like the oil obtained as a residue in the purification of caprylic alcohol with potash (p. 184). (Bouis.) — 5. It reduces ammoniacal nitrate of *silver* and forms a metallic mirror. — 6. With *pentachloride of phosphorus* it forms the compound  $C^{16}H^{16}Cl^3$ . (Limpricht.)

*Combinations.* Caprylic aldehyde does not dissolve in water. (Bouis.)

It combines with the alkaline bisulphites, forming crystalline compounds. (Limpricht.) No elevation of temperature takes place during their formation. The compounds are insoluble in aqueous solutions of the alkaline bisulphites, and are decomposed by water. (Bouis.) The compounds of *cænanthol* with the alkaline bisulphites (xii, 449) give rise, according to Bouis, to an elevation of temperature whilst they are forming, and are decomposed by acids and by carbonate of soda, but not by water.

*Sulphite of Caprylic Aldehyde and Potash.* — When caprylic aldehyde is shaken up with a concentrated aqueous solution of bisulphite of potash, the liquid becomes filled with crystals. These are pressed between paper, washed with alcohol and dried over sulphuric acid. (Limpricht.)

The salt cannot be recrystallised. It evolves sulphurous acid on exposure to the air. On dissolving it in water, it yields caprylic aldehyde.



				Limpricht.
KO .....	47.2	...	18.3	20.10
2 SO <sup>2</sup> .....	64	...	24.9	26.60
16 C .....	96	...	37.8	35.16
18 H .....	18	...	7.0	6.67
4 O .....	32	...	12.0	11.47
<hr/>				
C <sup>16</sup> H <sup>16</sup> O <sup>2</sup> + NaO <sup>2</sup> SO <sup>2</sup> + 2Aq ....	257.2	...	100.0	100.00

According to Limpricht, the compound was contaminated with bisulphite of potash, which had lost a portion of its sulphurous acid.

*Appendix to Caprylic Aldehyde.*

**Methyl-ænanthal.**

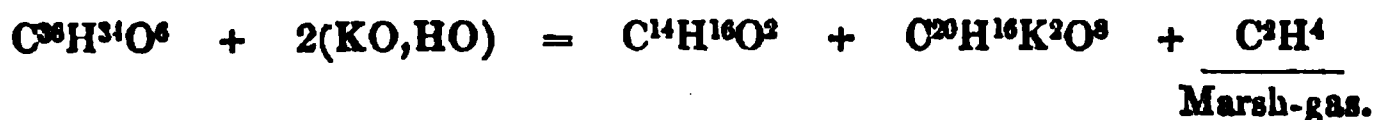


STÄDELER. *J. pr. Chem.* 72, 246.

*Formation.* By distilling a mixture of acetate and ænanthylate of soda. — 2. The product regarded by Limpricht and by Bouis as caprylic aldehyde (p. 187), is, according to Städeler, methylænanthal, its formation being represented by the equation:



And the simultaneous production of ænanthylic alcohol by the equation :



*Preparation.* 1. Equivalent quantities of acetate and ænanthylate of soda are dissolved in water; the solution is evaporated during constant stirring; and the residue is mixed with one-third of its bulk of chalk and distilled. The acid distillate is washed with soda, then with water, and rectified; and the portion which has passed over between 106° and 180° (amounting to three-fourths of the whole) is shaken with bisulphite of soda. A transparent gelatinous mass is thus formed, which, after 24 hours (when it has become opaque and solid), is pressed between paper, repeatedly triturated with alcohol, and again pressed. It is then warmed with carbonate of soda, whereby two strata are formed, the upper of which is decanted, dried over chloride of calcium, and rectified, the portion which distils at 171° being collected apart.

*Properties.* Thin, colourless liquid of sp. gr. 0.817 at 23°, boiling between 171° and 171.5°. Its smell recalls that of oil of rue; its taste is similar, and slightly burning. It makes grease-spots on paper. Neutral.

				Städeler.
16 C .....	96	...	75.00	74.78
16 H .....	16	...	12.50	12.47
2 O .....	16	...	12.50	12.75
<hr/>				
C <sup>16</sup> H <sup>16</sup> O <sup>2</sup> .....	128	...	100.00	100.00

Isomeric or identical with caprylic aldehyde.

It does not become acid on exposure to the air, even in presence



of platinum-black. When heated, it burns with a luminous yellow flame. It mixes with sulphuric acid and evolves heat, and is precipitated by water from the yellow solution apparently unchanged. It behaves like caprylic aldehyde with ammonia, potash, oxide of silver, and chromic acid.

Methylœnanthal is insoluble in water, but mixes with alcohol and with ether in all proportions.

### Caprylic Acid.



LERCH. *Ann. Pharm.* 49, 223.

FEHLING. *Ann. Pharm.* 53, 400.

ILJENKO & LASKOWSKY. *Ann. Pharm.* 55, 87.

GOTTLIEB. *Ann. Pharm.* 57, 63.

T. REDTENBACHER. *Ann. Pharm.* 59, 51; 57, 145.

SCHNEIDER. *Ann. Pharm.* 70, 118.

ALEX. MÜLLER. *J. pr. Chem.* 56, 103.

ROWNEY. *Chem. Soc. Qu. J.* 5, 22; *J. pr. Chem.* 56, 246.

RAILTON. *Chem. Soc. Qu. J.* 6, 205; *Pharm. Centr.* 1854, 256.

BOUIS. *N. Ann. Chim. Phys.* 44, 122; 48, 99.

Discovered by Lerch in 1844.

*Sources.* Caprylic acid exists as a conjugated compound in butter from cow's milk (Lerch); in cocoa-nut fat (Fehling); in Limburg cheese (Iljenko & Laskowsky); in human fat (hence also in perspiration.) (Lerch, *Ann. Pharm.* 59, 57.) In beet-root fusel-oil (A. Müller, Fehling; Dingler, *Pol. Jour.* 130, 77); in that portion of Scotch fusel-oil which distils over between  $190^{\circ}$  and  $220^{\circ}$ , in combination with oxide of ethyl or of amyl (Rowney); in the fusel-oil from rice or maize-spirit. (Wetherill, *Pharm. Centr.* 1854, 271.)

*Formation.* In the oxidation of caprylic alcohol with nitric acid (Bouis), or by heated oxygen (Railton); in the oxidation of caprylic aldehyde. (Bouis.)

In the dry distillation of oleïc acid or of fats containing oleïn (Gottlieb); in the oxidation of oleïc acid by strong nitric acid (Redtenbacher); in the oxidation of the more volatile part of the distillate obtained from rape-oil by nitric acid. (Schneider.) — It is formed together with œnanthylic acid and other acids, in the oxidation of oil of rue. (Cahours, *Compt. rend.* 31, 143), and of Chinese-wax (Buckton, *Chem. Soc. Qu. J.* 10, 166) by nitric acid. — In the decomposition of Demarçay's choloidic acid with nitric acid. (Redtenbacher, *Ann. Pharm.* 57, 145); also, together with many other volatile acids, in the putrefaction of yeast. (Al. Müller, *J. pr. Chem.* 70, 66; O. Hesse, *J. pr. Chem.* 71, 473.)

*Preparation.* 1. From butter of cow's milk. The mixture of caprylate and caprate of baryta, obtained in the preparation of butyrate of baryta, as described at x, 85, is dissolved completely in boiling water, and the solution is filtered boiling, whereby the filtrate becomes filled on cooling with scales of caprate of baryta having a fatty lustre; these crystals are filtered off and the mother-liquor is reduced to one-fourth of its volume, whereupon an additional quantity of caprate of baryta crystallises out. The caprylate of baryta remains in solution, and by

allowing the mother-liquor to evaporate in the sun, it is obtained in grains and nodules, of the size of a poppy-seed. The crystals are purified by recrystallisation. (Lerch.) (For preparation of the acid from the baryta-salt see below.) — 2. From cocoa-nut fat. The caprylate of baryta obtained, according to xi, 415, is decomposed by a dilute acid, the caprylic acid rising to the surface in the form of an oil. The oil is decanted, washed with a little water and distilled by itself, when it leaves a small residue. (Fehling.) — 3. Fifty pounds of strongly smelling Limburg cheese are cut into fine pieces and distilled for several days with water, or as long as the distillate continues to smell of cheese (to prevent the cheese from burning, fresh water is added from time to time, and the whole is stirred up). The turbid, strongly alkaline distillate is supersaturated with sulphuric acid, again distilled, and the distillate is neutralised with baryta-water, whereby valerate of baryta and a little butyrate of baryta are obtained. When the cheese which remains in the still is saponified with potash, and the soap decomposed with sulphuric acid, it yields, if again distilled with the same precautions, an acid distillate which is to be mixed with baryta-water and evaporated down as long as crystals continue to form. This salt, after being separated from the mother-liquor which contains butyrate and valerate of baryta, dissolves for the most part on boiling with 7 parts of water, and thus yields a solution of butyrate and caproate of baryta, and a residue of caprylate and caprate of baryta, which may be separated by crystallisation as in the first method (Iljenko & Laskowsky.) — 4. Oleic acid or fats containing olein are submitted to dry distillation; the distillate containing volatile acids and hydrocarbons is digested with dilute aqueous carbonate of soda, and rapidly evaporated in order to drive off the hydrocarbons; and the tolerably concentrated solution is decomposed in a retort with tartaric acid and distilled. The distillate saturated with baryta and treated according to 1, yields first caprate and then caprylate of baryta, and a little uncrySTALLISABLE mother-liquor, probably containing valerate and butyrate of baryta.

*Properties.* Colourless. Solidifies below  $12^{\circ}$ , and melts between  $14^{\circ}$  and  $15^{\circ}$ ; when slowly cooled, it crystallises in laminæ resembling cholesterolin. At ordinary temperatures it is greasy, and crystallises at about  $10^{\circ}$  in fine needles. (Lerch.) Smells like perspiration (Lerch, Redtenbacher); has a faint unpleasant odour, which increases on warming, and then resembles that of sebacic acid; it is very irritating to the eyes. (Fehling.) The aqueous solution tastes strongly acid and sharp. (Lerch.) Boils at  $236^{\circ}$ , the boiling point rising to  $238^{\circ}$ , and ultimately to  $240^{\circ}$ . Sp. gr. = 0.911 at  $20^{\circ}$ . Vapour-density = 5.31. (Fehling.)

					Fehling.
16 C	.....	96	....	66.67	..... 66.15
16 H	.....	16	....	11.11	..... 11.27
4 O	.....	32	....	22.22	..... 22.58
<hr/>					
$C^{16}H^{16}O^4$	.....	144	....	100.00	..... 100.00
		Vol.		Density.	
C-vapour	.....	16	.....	6.6560	
H-gas	.....	16	.....	0.5544	
O-gas	.....	2	.....	2.2186	
<hr/>					
Caprylic acid vapour	....	2	.....	9.4290	
		1	.....	4.7145	

*Decompositions.* Caprylic acid decomposes slightly at a high temperature, and leaves a clear brownish residue, which accounts for the vapour-density coming out too high. (Fehling.) Heated with 4 pts. of hydrate of lime, it yields gaseous and liquid hydrocarbons of the formula  $C^nH^n$ . (Cahours, *Compt. rend.* 31, 144.)

Caprylic acid is sparingly soluble in water. (Lerch.) It dissolves in 400 pts. of water at  $100^\circ$ , and at  $110^\circ$  separates out again almost completely in crystals. (Fehling.)

The salts of caprylic acid are but sparingly soluble, with the exception of those of ammonia, potash, and soda. (Lerch.)

*Caprylate of Baryta.* — *Preparation* (p. 191). Crystallises on evaporation from its hot solutions in fine scales having a fatty lustre; by spontaneous evaporation of the solution, in white chalky grains of the size of a poppy-seed. (Lerch.)

Fine crystalline grains and geodes resembling poppy-seeds; when obtained by spontaneous evaporation, very hard prisms having a fatty lustre and more than a quarter of an inch long. (Redtenbacher.) It is very bulky. After drying it has a fatty lustre. (Fehling.) Permanent in the air at the ordinary temperatures and at  $100^\circ$ . (Lerch.)

When distilled alone at a temperature which is gradually raised to a red heat, the salt yields a residue containing a quantity of charcoal, and a distillate consisting of acid water, and a yellow oil which smells of acetone and afterwards deposits white flakes. The salt rapidly heated with hydrate of lime, yields a distillate which resembles butter, and contains caprylone and an oil, probably an aldehyde. (Guckelberger, *Ann. Pharm.* 69, 202.) In contact with oxychloride of phosphorus, it forms caprylic anhydride. (Chiozza, *Ann. Pharm.* 85, 229.)

Dissolves with difficulty in water. (Lerch.) Dissolves in 106.6 pts. of water at  $10^\circ$ , in 50 pts. at  $100^\circ$ . (Fehling.) The solution does not decompose on exposure to the air. (Lerch.)

Perfectly insoluble in alcohol and in ether.

					Lerch.		Fehling.		Iljenko & Laskowsky.
16 C	.....	96	....	45.37	.....	45.47	....	45.28	.... 45.24
15 H	.....	15	....	7.09	.....	7.10	....	7.28	.... 7.16
3 O	.....	24	....	11.34	.....	11.42	....	11.40	.... 11.67
BaO	.....	76.6	....	36.20	.....	36.01	....	36.04	.... 35.93
<hr/>									
$C^{16}H^{16}BaO^4$	.....	211.6	....	100.00	.....	100.00	....	100.00	.... 100.00

						Redtenbacher.	Rowney.
16 C	.....	96	....	45.37	.....	45.51	.... 45.28
15 H	.....	15	....	7.09	.....	7.22	.... 7.35
3 O	.....	24	....	11.34	.....	11.19	.... 11.24
BaO	.....	76.6	....	36.20	.....	36.08	.... 36.13
<hr/>							
$C^{16}H^{16}BaO^4$	.....	211.6	....	100.00	.....	100.00	.... 100.00

According to Gottlieb, the salt contains 36.5 per cent. of baryta; according to Redtenbacher, 35.95; according to Müller, 36.3; and according to Bonis 36.0

*Caprylate of lead* is precipitated from the aqueous solution of the baryta-salt by nitrate of lead. (Lerch.)

White precipitate, permanent in the air. Melts below 100°. Sparingly soluble in water. (Lerch.)

				Lerch.
16 C	.....	96	.... 38·87	..... 39·08
15 H	.....	15	.... 6·07	..... 6·17
3 O	.....	24	.... 9·72	..... 9·28
PbO	.....	112	.... 45·34	..... 45·47
<hr/>				
C <sup>16</sup> H <sup>15</sup> PbO <sup>4</sup>	.....	247	.... 100·00	..... 100·00

*Caprylate of Silver.* — Caprylate of baryta forms a white precipitate with nitrate of silver. (Lerch, Redtenbacher.)

White (Lerch); curdy; does not blacken at 100° (Redtenbacher); precipitated from hot alcohol on cooling as a white powder containing 46·29 per cent. of oxide of silver. (Schneider.)

Nearly insoluble in water (slightly soluble according to Redtenbacher). Soluble in ammonia and in acids. (Schneider.)

				Lerch.	Gottlieb.	Redtenbacher.
16 C	.....	96	.... 38·24	..... 38·14	.... 38·43	.... 38·55
15 H	.....	15	.... 5·97	..... 6·05	.... 6·03	.... 6·01
3 O	.....	24	.... 9·56	..... 9·68	.... 9·09	.... 9·22
AgO	.....	116	.... 46·23	..... 46·13	.... 46·45	.... 46·22
<hr/>						
C <sup>16</sup> H <sup>15</sup> AgO <sup>4</sup>	.....	251	.... 100·00	..... 100·00	.... 100·00	.... 100·00

Caprylic acid mixes with *alcohol* and with *ether* in all proportions. (Fehling.)

### Sulphide of Capryl.



BOUIS. *N. Ann. Chim. Phys.* 44, 137.

*Ether caprylsulphydrique, Schwefelprylafer.*

When an alcoholic solution of monosulphide of sodium is heated with iodide of capryl until the mixture becomes turbid, the sulphide of capryl, being insoluble in alcohol saturated with sulphide or iodide of sodium, separates in the form of an oil.

Sulphide of capryl is a liquid, lighter than water, and having an unpleasant odour. Decomposes when heated. Slightly soluble in alcohol.

### Iodide of Capryl.



WILLS. *Chem. Soc. Qu. J.* 6, 307; *N. Ann. Chim. Phys.* 41, 103.

SQUIRE. *Chem. Soc. Qu. J.* 7, 108.

BOUIS. *N. Ann. Chim. Phys.* 44, 131.

*Ether capryliodhydrique, Iodcapryl, Iodprylafer.*

*Preparation.* 1. Iodine is dissolved in an equal weight of caprylic  
VOL. XIII. 0

alcohol and the solution is digested with phosphorus till the former becomes colourless. (Squire.) — 2. Small portions of phosphorus and iodine are added alternately to caprylic alcohol, care being taken to avoid an excess of phosphorus, which would form red iodide of phosphorus (to 100 pts. of the alcohol, 50 iodine and 6 phosphorus are taken). On distilling the strongly fuming liquid, water passes over first, then a liquid lighter than water, containing a quantity of caprylene, and finally the boiling point rises to  $200^{\circ}$ , and a beautiful violet-coloured liquid distils over together with vapour of phosphorus, phosphoric acid, and phosphoretted hydrogen, leaving a residue of red phosphorus and a syrup. The distillate is washed with carbonate of soda and afterwards with water; it is then submitted to fractional distillation, whereby iodide of capryl is obtained at  $210^{\circ}$ . (Bouis.)

**Properties.** Iodide of capryl is an oily liquid, smelling of oranges. It boils at  $210^{\circ}$  with decomposition, turning deep red from free iodine (Bouis); between  $191^{\circ}$  and  $196^{\circ}$  (Wills); at  $193^{\circ}$ . (Squire.) Sp. gr. = 1.81 at  $16^{\circ}$ . (Bouis.)

					Bouis.
16 C	.....	96	...	40.1	..... 40.66
17 H	.....	17	...	7.1	..... 7.30
I	.....	126	...	52.8	..... 52.64
<hr/>					
$C^{16}H^{17}I$	.....	239	...	100.0	..... 100.60

**Decompositions.** Iodide of capryl turns red on exposure to light. (Bouis, Wills.) Decomposes by boiling, and yields hydrocarbons and hydriodic acid. (Squire.) Burns with a smoky flame. (Bouis.)

Heated with alcoholic ammonia, it forms hydriodate of caprylamine (Squire, Cahours, Bouis); with excess of iodide of capryl, bicaprylamine and tercaprylamine are likewise produced. (Bouis.)

Behaves with sodium (or potassium) like chloride of capryl (p. 196.) (Bouis.)

Iodide of capryl heated with monosulphide of sodium in alcoholic solution, forms sulphide of capryl and iodide of sodium. (Bouis.) Heated with mercury, it forms green, insoluble, mercurous iodide, which dissolves when the liquid is heated, and crystallises on cooling, until after prolonged action, caprylene is formed and hydrogen evolved. (Bouis.)



An alcoholic solution of iodide of capryl precipitates silver-salts, forming insoluble iodide of silver together with the caprylic ether corresponding to the acid of the silver-salt.

### Bromide of Capryl.



MOSCHNIN. *Ann. Pharm.* 87, 117.

BOUIS. *N. Ann. Chim. Phys.* 44, 130.

*Ether caprylbromhydrique, Bromcapryl, Bromprylafer.*

**Preparation.** 1. Five pts. of bromine are dissolved in 8 pts. of caprylic alcohol, the solution treated with phosphorus till it becomes colourless,

and then distilled. The distillate is washed with water, then with dilute carbonate of soda, and again with water, and dried over chloride of calcium. (Moschnin.) — 2. A piece of phosphorus is placed in caprylic alcohol, and bromine gradually added till the phosphorus has disappeared; more phosphorus is then added as long as the liquid is decolorised. The liquid is warmed to expel the hydrobromic acid, then distilled, and the product which passes over at  $190^{\circ}$  is collected, washed with dilute carbonate of soda, and then rectified alone. (Bouis.)

Bromide of capryl is an oily liquid, having a strong narcotic odour (Moschnin); smells of oranges, like chloride of capryl. (Bouis.) Heavier than water. Boils, with decomposition, at  $190^{\circ}$ . (Bouis.) Leaves a carbonaceous residue when distilled. The yellowish distillate excites tears, and contains less bromine than bromide of capryl; when treated with water, it loses its colour and becomes lighter than water. (Moschnin.) Bromide of capryl burns with a smoky flame bordered with green. (Bouis.)

With potassium or sodium it behaves like chloride of capryl. (Bouis.)

Heated with potash, it forms bromide of potassium and caprylic alcohol. (Moschnin.)

Bromide of capryl precipitates silver-salts in alcoholic solution, but more slowly than the iodide. (Bouis.)

Insoluble in water, soluble in alcohol.

### Chloride of Capryl.



BOUIS. *N. Ann. Chim. Phys.* 44, 128.

M. BERTHELLOT. *Compt. rend.* 44, 1350; *Ann. Pharm.* 104, 185.

*Ether caprylchlorhydrique, Chorcapyrl, Chlorpyrlafer.*

**Formation.** 1. By the action of hydrochloric acid on caprylic alcohol. (Bouis.) — 2. By the action of pentachloride of phosphorus on caprylic alcohol. (Bouis.) — 3. By the action of hydrochloric acid upon caprylene (p. 181). (Berthelot.)

**Preparation.** 1. Caprylic alcohol is saturated with gaseous hydrochloric acid, the absorption being attended with evolution of heat; or the alcohol is mixed with concentrated fuming hydrochloric acid and the mixture is heated in a sealed tube to  $120^{\circ}$  or  $130^{\circ}$ . By this treatment only a portion of the alcohol is converted into chloride. — 2. Caprylic alcohol is poured into a long-necked flask, which is cooled with water; pentachloride of phosphorus is added in small portions and heat is applied, if no more action ensues in the cold, until the liquid distils over. In order to decompose the oxychloride of phosphorus, the distillate is cautiously mixed with water, and the chloride of capryl, which floats on the liquid is washed, first with water containing soda, then with pure water, and rectified. (Bouis.)

**Properties.** Colourless liquid. Boils at  $175^{\circ}$ , but the temperature

## 196 CONJUGATED COMPOUNDS CONTAINING THE NUCLEUS $C^{16}H^{16}$ .

risers towards the end of the distillation. Lighter than water. Smells very much like oranges. (Bouis.)

					Bouis.
16 C	.....	96	...	64.64	..... 64.52
17 H	.....	17	...	11.44	..... 11.82
Cl	.....	35.4	...	23.92	..... 24.30
<hr/>					
$C^{16}H^{17}Cl$	.....	148.4	...	100.00	..... 100.14

Chloride of capryl burns with a smoky flame bordered with green, and forms hydrochloric acid.

It does not precipitate salts of silver.

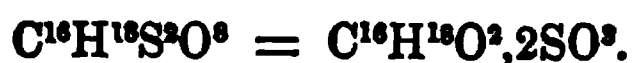
In contact with sodium or potassium in the cold, it yields capryl  $C^{16}H^{17}$ .

On heating chloride of capryl with sodium, the metal assumes a violet colour, swells up violently with elevation of temperature, and evolves hydrogen. Chloride of sodium is then formed, which by absorbing the liquid makes the latter pasty. If the liquid (containing less chlorine) obtained by the distilling this product, be placed in a second retort together with sodium, the violet colour again appears; and if the operation be repeated till the distillate is free from chlorine, it is found to consist of pure caprylene:



### *Conjugated Compounds containing the nucleus $C^{16}H^{16}$ .*

#### **Sulphocaprylic Acid.**



BOUIS. *Compt. rend.* 33, 144; *N. Ann. Chim. Phys.* 44, 124.

MOSCHNIN. *Ann. Pharm.* 87, 114.

*Preparation.* Two pts. of caprylic alcohol are slowly mixed with one part of sulphuric acid, the whole being cooled in order to prevent evolution of sulphurous acid, and the mixture is allowed to stand in a moderately warm place. After 6 or 7 days, two strata are formed, the lower consisting of the excess of sulphuric acid, the upper of sulphocaprylic acid. (Moschnin.) When equal parts of sulphuric acid and caprylic alcohol are employed, sulphurous acid is generally evolved, and the mixture blackens if not properly cooled. It is therefore preferable to use Nordhausen sulphuric acid, which produces no blackening and less evolution of sulphurous acid; care must however be taken to avoid continuing the action too long. (Bouis.) After being saturated with carbonate of lime, baryta or lead, the liquid yields soluble salts. Free sulphocaprylic acid is obtained by exactly decomposing the baryta-salt with dilute sulphuric acid, or by decomposing the lead-salt with sulphuretted hydrogen, and evaporating the liquid in vacuo. (Bouis.)

Sulphocaprylic acid is a colourless syrupy liquid, which decomposes and chars when heated. (Bouis.)



It dissolves very readily in water; the solution has a strong acid reaction, and is resolved by heat into caprylic alcohol and aqueous sulphuric acid. (Bouis, Moschnin.)

*Sulphocaprylate of Potash.* — 1. The product obtained by the action of sulphuric acid upon caprylic alcohol is saturated with carbonate of potash, evaporated to dryness, and the residue is extracted with boiling alcohol, which leaves the sulphate of potash undissolved and deposits sulphocaprylate of potash in shining laminæ on cooling. — 2. Sulphocaprylate of baryta is exactly decomposed by carbonate of potash.

White, shining, unctuous to the touch. Tastes exceedingly bitter, and then sweet.

					Bouis.
16 C	.....	96	...	37.3	..... 37.14
18 H	.....	18	...	6.9	..... 6.92
SO <sup>3</sup>	.....	40	...	15.7	
KO, SO <sup>3</sup>	.....	87.2	...	33.9	..... 34.06
2 O	.....	16	...	6.2	
<hr/>					
C <sup>16</sup> H <sup>17</sup> KO <sup>2</sup> , 2SO <sup>3</sup> + Aq					.... 257.2 .... 100.0

At 100° it becomes red and acid. Burns when heated, leaving a residue of sulphate of potash, and forms sulphate of potash and caprylic alcohol when heated with aqueous carbonate of potash. Distilled with cyanate of potash, it yields a fluid and a crystallisable substance, which form caprylamine when treated with potash, and are in all probability cyanate and cyanurate of capryl. (Bouis.)

*Sulphocaprylate of Baryta* is obtained by saturating crude sulphocaprylic acid with carbonate of baryta, filtering, and carefully evaporating the solution over a water-bath until it crystallises. It forms flexible nacreous crystals, when obtained by cooling the hot solution (Moschnin); sometimes fine needles, when crystallised from alcohol. (Bouis.) In vacuo only nodular masses are formed. (Moschnin.) The salt tastes strongly bitter and then sweet. The crystals give off 6.67 per cent. of water (2 At. = 6.09 per cent.) in vacuo over sulphuric acid, and then yield 42.06 per cent. of sulphate of baryta. (Moschnin.) (C<sup>16</sup>H<sup>17</sup>BaO<sup>2</sup>, 2SO<sup>3</sup> requires 42 per cent.) The crystallised salt contains 25.12 per cent. of baryta, corresponding to the formula C<sup>16</sup>H<sup>17</sup>BaO<sup>2</sup>, 2SO<sup>3</sup> + 3Aq. (Calculated 25.15 per cent. BaO). (Bouis.)

The dry salt, if allowed to stand for a long time in vacuo, becomes red and emits a strong odour which excites coughing. It blackens at 100° and decomposes without melting. Burns with a clear blue flame; leaving a residue of sulphate of baryta. (Moschnin.)

*Sulphocaprylate of Lime* crystallises in white tablets, tastes bitter and feels like soap. (Moschnin.)

Aqueous sulphocaprylic acid dissolves iron and zinc, with evolution of hydrogen.

Sulphocaprylic acid forms with oxide of lead two salts probably containing 1 and 2 atoms of oxide of lead to 1 atom of acid. — *a*. The neutral salt, obtained by saturating the acid with carbonate of lead, crystallises readily and has an acid reaction. — *b*. The basic salt is



obtained as a transparent mass by digesting the neutral salt with oxide of lead and evaporating the colourless alkaline solution. Its solution absorbs carbonic acid from the air and is converted into the neutral salt. (Moschnin.)

Sulphocaprylic acid is readily soluble in alcohol. (Bouis.)

### Nitrate of Capryl



BOUIS. *N. Ann. Chim. Phys.* 44, 136.

*Ether capryloxotique, Salpetercaprylester.*

*Preparation.* Iodide of capryl is dissolved in boiling alcohol, an excess of alcoholic nitrate of silver added to the solution, and the precipitated iodide of silver separated by filtration; on adding water to the alcoholic solution, the nitrate of capryl is separated as an oil.

Smells like the acetate of capryl. Lighter than water. Begins to boil at  $80^\circ$ , then becomes black, while the temperature rises, and yields a strongly smelling acid distillate with a residue of charcoal.

Burns with a luminous flame.

Boiled with alcoholic potash, it yields crystals of nitre and caprylic alcohol.

Nitrate of capryl is soluble in alcohol.

### Methyl-caprylic Ether.



WILLS. *Chem. Soc. Qu. J.* 6, 314; *N. Ann. Chim. Phys.* 41, 103.

BOUIS. *N. Ann. Chim. Phys.* 44, 139.

*Methyl-caprylæther, Octylate of Methyl, Methylate of Octyl.*

Formed by the action of iodide of methyl upon caprylate of sodium. (Wills.)



Methyl-caprylic ether is a thin mobile liquid having a strong odour. Boils between  $160.5^\circ$  and  $161^\circ$ . Sp. gr. = 0.830 at  $16.5^\circ$ . Vapour-density, about 4.2. (Wills.)

According to Wills, who regards caprylic alcohol as œnanthyllic alcohol, the compound is methyl-œnanthyllic ether,  $C^{16}H^{18}O^2 = C^2H^2O, C^{14}H^{16}O$ . The analysis gave 73.8 p. c. C and 13.8 H, the formula  $C^{18}H^{20}O^2$  requiring 75.0 C and 13.9 H, while  $C^{16}H^{18}O^2$  requires 74.7 C and 13.7 H. The vapour-density calculated from  $C^{18}H^{20}O^2$  is 4.99 and from  $C^{16}H^{18}O^2$ , it is 4.5. The substance was not obtained pure.

Insoluble in water, readily soluble in alcohol and in ether.

## Caprylate of Methyl.



**FEHLING.** *Ann. Pharm.* 58, 405.

***Caprylsäures methoxyd, Caprylformester.***

2 pts. of caprylic acid is dissolved in 2 pts. of wood-spirit and 1 pt. of sulphuric acid is added. The mixture becomes turbid and soon separates the ether, which is decanted, washed with water and dried with chloride of calcium.

Smells highly aromatic and at the same time of wood-spirit. Sp. gr. = 0.882. Vapour density = 5.48.

					<b>Fehling.</b>			<b>Vol.</b>	<b>Density.</b>
<b>18 C</b>	....	<b>108</b>	....	<b>68·35</b>	....	<b>68·38</b>	<b>C-vapour .....</b>	<b>18 ....</b>	<b>7·4880</b>
<b>18 H</b>	....	<b>18</b>	....	<b>11·39</b>	....	<b>11·42</b>	<b>H-gas .....</b>	<b>18 ....</b>	<b>1·2474</b>
<b>4 O</b>	....	<b>32</b>	....	<b>20·26</b>	....	<b>20·20</b>	<b>O-gas .....</b>	<b>2 ....</b>	<b>2·2186</b>
<hr/>									
<b>C<sup>18</sup>H<sup>18</sup>O<sup>4</sup></b>		<b>158</b>	....	<b>100·00</b>	....	<b>100·00</b>	<b>Vapour .....</b>	<b>2 ....</b>	<b>10·9540</b>
								<b>1 ....</b>	<b>5·4770</b>

## Ethyl-caprylic Ether.



**WILLS.** *Chem. Soc. Qu. J.* 6, 312; *N. Ann. Chim. Phys.*, 41, 103.

***Aethyl-capryläther, Vinecapryläther, Octylate of Ethyl, Ethylate of Octyl.***

Formed by the action of caprylate of sodium upon an equivalent quantity of iodide of ethyl.

Colourless, mobile liquid, having an odour different from that of caprylic alcohol. Boils at  $177^{\circ}$ . Sp. gr. = 0.791 at  $16^{\circ}$ . Vapour-density = 5.095.

Calculation. I.				Calculation II.				Wills.
20 C	.....	120	.... 75·95	18 C	.....	108	.... 75·00	..... 75·16
22 H	.....	22	.... 13·92	20 H	.....	20	.... 13·88	..... 14·44
2 O	.....	16	.... 10·13	2 O	.....	16	.... 11·12	..... 10·40
<hr/>				<hr/>				
$C^{20}H^{22}O^2$	....	158	.... 100·00	$C^{18}H^{20}O^2$	....	144	.... 100·00	..... 100·00

	Vol.		Density.		Vol.		Density.
C-vapour .....	20	.....	8·3200	Or :	18	.....	7·4880
H-gas .....	22	.....	1·5246		20	.....	1·3860
O-gas .....	1	.....	1·1093		1	.....	1·1093
<hr/>							
Vapour .....	2	.....	10·9539		2	.....	9·9833
			5·4769		1	.....	4·9916

According to Wills, (calc. ii) the compound is ethyl-cenanthylic ether. This view agrees best with the analysis and the vapour-density, and is furthermore in accordance with the recent investigations of Städeler on the alcohol obtained from castor-oil (p. 182).

**Burns with a luminous flame.**

**Insoluble in water, readily soluble in alcohol and in ether.**

**Acetate of Capryl.**

Bouis. *N. Ann. Chim. Phys.* 44, 135.

*Ether-caprylacétique, Essigcaprylester.*

*Formation and Preparation.* 1. By distilling caprylic alcohol with acetic acid. — 2. When hydrochloric acid gas is passed into a solution of caprylic alcohol in acetic acid, acetate of capryl is formed and may be separated by water. — 3. A solution of caprylic alcohol in sulphuric acid is distilled with acetate of soda (the liquid while hot assuming a transient violet colour); the distillate is rectified after being well washed and dried; and the liquid which passes over at the boiling point of the ether is collected separately. — 4. An alcoholic solution of iodide of capryl is boiled with crystallised acetate of silver; the iodide of silver is filtered off; and the alcohol evaporated from the filtrate on a water-bath; or the ether which has formed is separated by water. On heating iodide of capryl with dry acetate of silver, the liquid turned red and a quantity of acetic acid was set free.

Liquid having a pleasant fruity odour. Boils at  $193^{\circ}$ . Lighter than water.

					Bouis.
20 C .....	120	...	69.76	.....	69.41
20 H .....	20	...	11.62	.....	11.86
4 O .....	32	...	18.62	.....	18.73
<hr/>					
$C^{20}H^{40}O^4$ .....	172	...	100.00	.....	100.00

Acetate of capryl burns with a bright flame. It is dissolved by sulphuric acid, and is precipitated from the solution by water; if the sulphuric acid is concentrated, formation of sulphurous acid and caprylene takes place, and water separates from the solution a red oil.

When boiled with potash, acetate of capryl is resolved into acetate of potash and caprylic alcohol.

Insoluble in water. Soluble in alcohol.

**Caprylone.**

G. GUCKELBERGER. *Ann. Pharm.* 69, 201.

*Preparation.* 1 pt. of caprylate of baryta is mixed with 2 pts. of hydrate of lime in a warmed retort and the mixture is heated rapidly over a naked charcoal fire to dull redness, so that if half an ounce of the salt is employed, the operation is over in 20 or 30 minutes. Dense white vapours are then evolved, which condense in the receiver, surrounded by

cold water, into a yellow oil, soon solidifying into a buttery mass. This substance is pressed between paper, which absorbs a dark yellow oil, and a white mass is ultimately left, which is washed with cold alcohol and crystallised from boiling alcohol.

*Properties.* White mass resembling Chinese-wax; crystallises from its solutions in needles having a silky lustre. It is tasteless and has a slight odour of wax. Melts at 40°, and when melted, solidifies at 38° into a crystalline mass. Lighter than water, but sinks in alcohol of sp. gr. 0·89. Boils at 178°, and distils without alteration.

					Guckelberger.
30 C	.....	180	....	79·64	..... 79·18
30 H	.....	30	....	13·27	..... 13·32
2 O	.....	16	....	7·09	..... 7·50
<hr/>					
C <sup>30</sup> H <sup>50</sup> O <sup>2</sup>	.....	226	....	100·00	..... 100·00

*Decompositions.* Caprylone is not acted upon by cold *nitric acid*, not even by the fuming acid. But at the melting point of caprylone, nitric acid of sp. gr. 1·4 acts violently upon it; and evolves vapours which, when passed through water, impart to it an ethereal odour. A dark yellow oil remains, which is freed from the acid by water. The oil is heavier than water, has a burning aromatic taste, and is nearly insoluble in water, but dissolves readily in aqueous alkalis. Its ammoniacal solution forms with silver-salts, and also with lead-salts, precipitates of the colour of yolk of egg. The silver-salt decomposes very rapidly, even in *vacuo*; it explodes at a gentle heat; hence the yellow oil is probably nitrocaprylic acid.

Caprylone is not acted upon by *potash*.

It does not reduce an ammoniacal solution of *silver*.

Insoluble in *water*.

Caprylone dissolves abundantly in *alcohol* of 80 per cent., and still more when the alcohol is hot, so that the solution becomes pasty on cooling.

Caprylone dissolves so abundantly in hot *wood-spirit* that the solution becomes pasty on cooling.

Dissolves readily in *ether*, and in oils both *volatile* and *fatty*.

### Caprylate of Ethyl.



FEHLING. *Ann. Pharm.* 53, 403.

*Caprylsaures Aethyloxyd, Caprylvinester.*

To a solution of 2 pts. of caprylic acid in 2 pts. of absolute alcohol, 1 pt. of sulphuric acid is added. The mixture immediately becomes turbid, and the ether separates from it in a few seconds. The product is freed from the acid by washing with water, and then dried over chloride of calcium.

## 202 CONJUGATED COMPOUNDS CONTAINING THE NUCLEUS $C^{16}H^{16}$ .

Caprylate of ethyl is a colourless, limpid liquid. It has a pleasant odour of pine apples. Sp. gr. = 0.8738 at 15°. Boils at 214°. Vapour-density = 6.100°.

				Fehling.
20 C .....	120	...	69.76	69.89
20 H .....	20	...	11.62	11.85
4 O .....	32	...	18.62	18.26
<hr/>				
$C^{20}H^{20}O^4$ .....	172	...	100.00	100.00

	Vol.	Density.
C-vapour .....	20	8.3200
H-gas .....	20	1.3860
O-gas .....	2	2.2186
<hr/>		
Caprylate of ethyl vapour .....	2	11.9246
	1	5.9623

Nearly insoluble in water, readily soluble in alcohol and in ether.

### Amyl-caprylic Ether.



WILLS. *Chem. Soc. Qu. J.* 6, 316; *N. Ann. Chim. Phys.* 41, 103.

*Amyl-octylic ether, Octylate of amyl, Amylate of octyl, Myle-capryläther.*

Formed by the action of caprylate of sodium upon iodide of amyl, and obtained with difficulty, by submitting the product to fractional distillation, as a colourless, mobile liquid, boiling between 220° and 221°. Sp. gr. = 0.608 at 20°. Vapour-density 6.57.

According to Wills, the substance is amyl-cenanthylic ether,  $C^{24}H^{26}O^2$ , which requires 77.4 C and 14.0 H. The formula  $C^{26}H^{26}O^2$  requires 78 C and 14 H. Analysis gave 77.0 C and 13.8 H. The calculated vapour-density of amyl-cenanthylic ether is 6.45, and of amyl-caprylic ether 6.93.

### Caprylic Anhydride.



CHIOZZA. *Ann. Pharm.* 85, 229.

*Anhydrous caprylic acid, Caprylic caprylate, Caprylate of capryl.*

Oxychloride of phosphorus acts readily upon caprylate of baryta, forming a doughy mass, from which ether free from alcohol extracts caprylic anhydride. The solution treated with weak potash and dried by chloride of calcium, leaves the anhydride when the ether is evaporated on the water-bath. Colourless, mobile oil, which when exposed to a freezing mixture, solidifies into a white mass, exhibiting a crystalline structure under the magnifying glass, and melting at a few degrees below 0°. Has a sickly odour, like that of carouba beans; when heated

it gives off an aromatic vapour, which strongly irritates the throat. Unctuous to the touch. Lighter than water. Boils at  $280^{\circ}$ , but the temperature rises to  $290^{\circ}$  towards the end of the distillation, while the residue becomes coloured and stinking, empyreumatic products pass over.

It becomes acid by prolonged exposure to *moist air*, forming caprylic acid. It is not changed by boiling water, even on distillation.

Heated with a moderately concentrated solution of *potash*, it yields caprylate of potash.

In contact with *aniline*, it becomes slightly heated, and solidifies in a few days into a buttery mass which is difficult to obtain pure.

*Oxygen-nucleus*  $C^{16}H^{14}O^2$ .

### Hydride of Suberyl. $C^{16}H^{14}O^2$ .

BOUSSINGAULT. *J. Chim. méd.* 12, 230; *J. pr. Chem.* 7, 211; *Ann. Pharm.* 19, 308.

TILLEY. *Mem. Chem. Soc.* 1, 1; *Ann. Pharm.* 39, 166; *Phil. Mag. J.* 18, 417.

*Suberone.*

*Formation and Preparation.* 1. Formed, together with hydrocarbons, by the action of lime upon suberic acid at a moderate heat. (Boussingault.) — 2. When suberic acid is distilled with caustic lime, an agreeably smelling, thick brown oil passes over; and on rectifying this oil till the boiling point rises to  $178^{\circ}$ , benzol passes over first, then hydride of suberyl, and a black pitchy mass remains in the retort. (Tilley.)

*Properties.* Colourless liquid. (Tilley.) Boils at  $186^{\circ}$  (Boussingault), at  $176^{\circ}$ . (Tilley.) Does not solidify at  $-12^{\circ}$ . Smells strongly aromatic (Boussingault); agreeably. (Tilley.) Vapour density = 4.392. (Boussingault.)

16 C .....	96	.....	76.19
14 H .....	14	.....	11.11
2 O .....	16	.....	12.70

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$C^{16}H^{14}O^2$ .....	126	.....	100.00
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					Boussingault.		Tilley.
14 C .....	84	....	75.00	.....	76.6	....	75.61
12 H .....	12	....	10.71	.....	10.8	....	11.19
2 O .....	16	....	14.29	.....	12.6	....	13.20

---

$C^{14}H^{12}O^2$ .....	112	....	100.00	.....	100.0	....	100.00
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The formula  $C^{16}H^{14}O^2$  does not explain the mode of formation of hydride of suberyl; neither does the formula  $C^{14}H^{12}O^2$  explain the formation of the accompanying products, or that of suberic acid, by the oxidation of hydride of suberyl with nitric acid. (Gerhardt, *Traité* 2, 732.)

*Decompositions.* 1. Hydride of suberyl is readily oxidised to suberic acid by nitric acid. (Boussingault.) In this reaction, another acid, crystallising in fine needles, is formed as well. (Tilley.) — 2. When chlorine gas is passed through hydride of suberyl, the liquid becomes heated, forms hydrochloric acid, blackens, and is completely decomposed if not cooled. When no more hydrochloric acid is formed, a thick oil of sharp, unpleasant odour remains, which may be freed from excess of chlorine by heating with carbonic acid gas. This oil cannot be distilled without decomposition, but blackens and decomposes when heated. When the chlorine-compound is dissolved in alcoholic potash and the solution diluted with water, a thick ethereal oil is precipitated, heavier than water, brown in colour, and possessing the odour, taste and other properties of benzoate of ethyl. (Tilley.)

### Appendix.

#### Cork-resin.

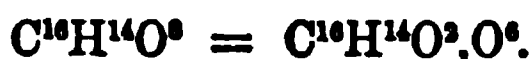
BOUSSINGAULT. *Institut. 4me année*, No. 142; abstr. *J. pr. Chem.* 7, 213; *J. Chim. Med.* 12, 230.

When ether is poured upon cork, it assumes a pale-yellow colour, and the solution deposits cork-resin on evaporation.  
Small needles.

Calculation according to Boussingault.				Boussingault.	
32 C	.....	192	....	84.95	..... 82.4
26 H	.....	26	....	11.50	..... 11.1
O	.....	8	....	3.55	..... 6.5
<hr/>					
$C^{22}H^{26}O$	.....	226	....	100.00	..... 100.0

Cork-resin is converted by nitric acid into oxalic acid and a wa (named cerin by Chevreul).

#### Suberic Acid.



BRUGNATELLI. *Crell. Ann.* 1787, 1, 145.

BOUILLON LAGRANGE. *Ann. Chim.* 23, 42; abstr. *Scher. J.* 6, 591; further: *J. Pharm.* 8, 107.

TROMMSDORF. *A. Tr.* 17, 2, 46.

CHEVREUL. *Ann. Chim.* 62, 323; also *N. Gehl.* 5, 379; further: *Ann. Chim.* 96, 182; also *Schw.* 16, 336.

BRANDES. *Schw.* 32, 393; 33, 83; 36, 263; further: *Ann. Pharm.* 9, 295; *N. Br. Arch.* 21, 319.

BUSSY. *J. Pharm.* 8, 107; 19, 425.

BOUSSINGAULT. *J. Chim. Med.* 12, 230; *J. pr. Chem.* 7, 211; *Ann. Pharm.* 19, 307.

HARFF. *N. Br. Arch.* 5, 303.

LAURENT. *Rev. scient.* 10, 123; *J. pr. Chem.* 27, 313; *Ann. Chim. Phys.* 66, 157.

BROMEIS. *Ann. Pharm.* 35, 89.

TILLEY. *Ann. Pharm.* 39, 166; *Phil. Mag. J.* 18, 417; *Mem. Chem. Soc.* 1, 1.

SACC. *Ann. Pharm.* 51, 222.

GERHARDT. *Compt. chim.* 1845, 178.

LAURENT & GERHARDT. *N. Ann. Chim. Phys.* 24, 184.

WIRZ. *Ann. Pharm.* 104, 261.

#### *Korksäure.*

*Formation.* By the action of nitric acid upon cork, paper (Brugnattelli, *A. Gehl.* 1, 340), elder-pith (Link [Chevreul opposes him]), the bark of trees, and linen rags (Berzelius, *Lehrbuch*, 3 Aufl. 8, 47). Also in the oxidation of oleic acid (Laurent), stearic acid (Bromeis), castor-oil (Tilley) and linseed-oil (Sacc) by nitric acid. — By treating hydride of suberyl with nitric acid.

*Preparation.* 1. Rasped cork is distilled with 6 pts. of nitric acid of 30° B. till only a small residue is left; this is placed in a porcelain dish and, while constantly stirred, evaporated to the consistence of honey. The mass is treated with boiling water which extracts suberic acid, rendered impure by artificial bitter, and leaves woody fibre together with wax. On evaporating and cooling the solution, the suberic acid separates and may be purified, either by repeated solution in hot water and cooling, or by boiling with powdered charcoal, or by combination with lime and precipitation by hydrochloric acid. Berzelius (*Lehrbuch*, 3rd Ed. 8, 48) recommends sublimation. (According to Brandes, 9.6 pts. of cork yield 1 pt. of suberic acid; according to Chevreul, 12 pts. of cork are required to yield that amount.)

2. The suberic acid obtained according to x, 464, is a mixture of that acid with an oil which is soluble in nitric acid, and with azelaic acid, which is soluble in water. The product is dissolved in hot water, whereby the oil is separated in drops, and the whole is allowed to stand at a temperature between 50° and 60° until all the oil, except a small portion which floats on the liquid, has settled to the bottom of the vessel. The solution is then decanted from the oil and left to cool, whereupon the suberic acid crystallises: it is collected on a filter, washed with cold water, and dried. In order to extract the azelaic acid, the powdered acid is placed in a flask and treated with 2 or 3 times its volume of ether, which dissolves all the azelaic acid and a large quantity of suberic acid besides. The residual suberic acid is boiled with pure nitric acid for two or three hours, allowed to crystallise by cooling, washed, and then obtained pure by solution in boiling water and crystallisation. (Laurent.)

3. Stearic acid is heated with nitric acid, which is renewed until all the stearic acid has disappeared and a clear solution is formed. This solution evaporated down to half its volume, solidifies in 24 hours to an almost solid mass, which is washed on a funnel with cold water (in order to remove the mother-liquor which contains succinic acid) then thrice recrystallised from hot water, pressed and dried. (Bromeis.)



4. Oleic acid is digested with nitric acid, renewed until no more action is perceptible. On cooling below  $0^{\circ}$ , the solution solidifies in 12 hours into a yellowish-white, soft mass, consisting almost entirely of suberic acid. The product is collected on a funnel, half closed with a piece of glass rod, and the mother-liquor containing pimelic, adipic, and lipic acids, together with an oil soluble in nitric acid, runs away, and leaves the suberic acid. This is washed with cold water, recrystallised four, five, six times from boiling water, then pressed and dried. (Bromeis.)

5. When 1 pt. of castor-oil is heated with 2 pts. of nitric acid diluted with its own bulk of water, and the boiling liquid is poured off from the solid residue, the solution on cooling deposits suberic acid, which is purified by boiling with nitric acid and repeated crystallisation. (Tilley.) If the dilute nitric acid is allowed to act rapidly upon the oil, a quantity of cœnanthylic acid passes over, and suberic acid remains in the residue; if, however, the whole is slowly heated, a quantity of prussic acid is formed together with a nitro-acid ( $C^{14}X^3H^{17}O^2$ ). (Bouis, *N. Ann. Chim. Phys.* 44, 92.)

6. One pt. of linseed-oil is heated with 2 pts. of commercial nitric acid diluted with 4 pts. of water, whereupon the oil first turns red and is then converted into a yellow resin; the liquid is decanted and the resin again treated with concentrated nitric acid, which is poured off after 4 or 5 hours and renewed. By a more prolonged action of nitric acid, the suberic acid is converted into an oil smelling of butyric acid. The product is crystallised 3 or 4 times from water, in order to remove the nitric acid, then dried between blotting paper, melted at a gentle heat, and distilled as rapidly as possible, a slight residue of charcoal then remaining. The distillate, which is rendered impure by a black resin, on which account it smells of acetone, is dissolved in boiling water; and the solution is purified with animal charcoal which has been washed with nitric acid, and filtered: pure suberic acid then crystallises out on cooling. (Sacc.)

7. The fatty acids of cocoa-nut-oil, of comparatively high atomic weight, which result from the decomposition of the soda-soap with sulphuric acid, and remain in the residue after the volatile acids have been distilled off, are boiled in a capacious retort with 3 pts. of commercial nitric acid. At first the whole boils quietly, giving off red and peculiarly smelling vapours, which violently attack the organs of respiration; but after the boiling has been continued for 14 days with fresh additions of nitric acid, a violent reaction sets in, abundant vapours are evolved (which may partly project the mass into the receiver) while the fatty acids, which at first solidified into a cake upon the nitric acid, partly settle to the bottom in the form of a thick viscid oil. The boiling is continued till the thick oil, which at first increased, is wholly converted into a white crystalline paste (for which about two months are requisite), and upon which nitric acid has but little action: the nitric acid is then distilled off as completely as possible, and the contents of the retort are dissolved in water. A yellow solution is thus produced which is rendered turbid by minute globules of oil, but on standing in a warm place deposits the oil and becomes clear. The solution is next poured off from the oil and evaporated on a water-bath until most of the nitric acid has been driven off, and the residue solidifies on cooling; the mass is redissolved in water; and the solution again evaporated as long as nitric acid goes off. The pasty crystalline mass is dissolved in 2 measures of hot

water; the white grains which form in the course of 12 hours are separated from the mother-liquor (in which pimelic, adipic, lipic, and succinic acids remain), and the liquid is further evaporated as long as detached grains, consisting of suberic acid, lepargylic acid, and a third acid continue to crystallise out, and until crystalline crusts, different from the grains, begin to form. The crude suberic acid thus obtained is washed with cold water, repeatedly recrystallised, and lastly crystallised from gently warmed alcohol until the mineral matter is removed; the recrystallisation is then continued, and the portions containing lepargylic acid which first crystallise out, are separated from the mother-liquor, which on further evaporation yields pure suberic acid.

*Properties.* Suberic acid separates from its aqueous solution on cooling partly as a white, opaque, granular powder, partly in confusedly crystalline cakes (Chevreul); in small needles which unite into masses like cauliflower-heads. (Sacc.) Melts at  $120^{\circ}$  (Bromeis), between  $123^{\circ}$  and  $124^{\circ}$  (Brandes), at  $124^{\circ}$  (Bussy); when introduced into capillary tubes it melts partially at  $120^{\circ}$ , and completely at  $128^{\circ}$  (Wirz); after drying at  $100^{\circ}$ , it melts without loss of weight. Solidifies in a fibrous mass (Chevreul), crystalline (Boussingault), radiated (Wirz); in a mass formed of beautiful, transparent, long (acuminated, according to Bromeis), crystalline needles. (Laurent.) (If the liquid portion be poured off, before the mass has completely solidified, a hollow space is found in the interior covered with brilliant needles.) (Bussy.) Volatilises in the air (above  $124^{\circ}$  according to Bussy) without residue, in white, suffocating vapours which smell of stearin (Bouillon, Chevreul); sublimes in closed vessels in needles half an inch long, and leaves only a trace of charcoal. (Chevreul.) Distils like the fatty acids when heated in a retort. (Bussy.) Condenses, when volatilised, in the upper part of the retort as an oil, which solidifies in an acicular mass on cooling. (Laurent.) Reddens litmus. Tastes slightly acid. Inodorous. Permanent in the air.

				Bouillon-Lagrange.	Bussy.	Brandes.				
16 C	.....	96	....	55.17	.....	58.33	....	55.79	....	55.41
14 H	.....	14	....	8.04	.....	7.67	....	7.98	....	8.36
8 O	.....	64	....	36.79	.....	34.00	....	36.23	....	36.23
<hr/>										
C <sup>16</sup> H <sup>14</sup> O <sup>8</sup>	.....	174	....	100.00	.....	100.00	....	100.00	....	100.00

				Bromeis.		Tilley.	Wirz.					
Boussingault.		Laurent.		a.	b.							
16 C	.....	55.1	....	55.77	....	56.72	....	55.09	....	55.97	....	54.50
14 H	.....	8.0	....	8.19	....	8.45	....	7.94	....	8.15	....	8.06
8 O	.....	36.9	....	36.04	....	34.83	....	36.97	....	35.88	....	37.44
<hr/>												
C <sup>16</sup> H <sup>14</sup> O <sup>8</sup>	.....	100.0	....	100.00	....	100.00	....	100.00	....	100.00	....	100.00

Bussy's and Brandes' suberic acid were obtained from cork; Laurent's and Bromeis' (a) from oleic acid and stearic acid (b); Tilley's from castor oil. Boussingault analysed the acid obtained by the oxidation of hydride of suberyl. — Compare also Brandes, *Ann. Pharm.* 9, 295.

Suberic acid heated with oxide of lead gives off 10.08 per cent. of water (Bussy); 10.73 per cent.. (Bromeis.)

*Decompositions.* 1. Suberic acid heated in glass flasks evolves

vapours which violently attack the organs of respiration, and condense into drops which become solid and crystalline. A carbonaceous residue is left. (Bromeis.) (See also page 206.)

2. Decomposed by prolonged boiling with *nitric acid* (Laurent), forming a volatile oil smelling of butyric acid. (Sacc.) Suberic acid is not altered by boiling for 8 hours with nitric acid, but retains the same composition; the remaining nitric acid yields a little more suberic acid on evaporation. (Bromeis.)

3. Distilled with 4 pts. of *binoxide of manganese*, 1 pt. of *sulphuric acid*, and 1 pt. of water, it yields an acid distillate containing formic acid, and when more strongly heated, a small quantity of a light yellow oil which solidifies on cooling. (Brandes.)

4. Destroyed by fuming *sulphuric acid*, with blackening and evolution of sulphurous acid gas. (Brandes.)

5. Heated with excess of *hydrate of lime*, it yields hydrocarbons and hydride of suberyl. (Boussingault.) When suberic acid is distilled with *quick lime*, a thick brown oil passes over containing Boussingault's hydride of suberyl and perhaps also benzol. (Tilley.)

6. Fused with *aniline*, it yields suberanilide and suberanilic acid. (Laurent & Gerhardt.)

*Combinations.* A. With Water. — The acid dissolves in 120 pts. of cold water (Bouillon), 80 pts. (Chevreul), 50 pts. (Fourcroy); in 100 pts. of water at  $9^{\circ}$ , in 86 pts. at  $12^{\circ}$  (Brandes), in 93.6 pts. at  $18^{\circ}$  (100 pts. of water dissolve 1.014 pts. of the acid) (Wirz); in 38 pts. of water at  $60^{\circ}$  (Chevreul), in 5 pts. of water at  $84^{\circ}$  (Brandes), and in 2 pts. of boiling water (Bouillon), 1.87 pts. (Brandes), separating from the last solution on cooling so that the whole solidifies. 100 pts. of the hot saturated solution cooled to  $18^{\circ}$  still contain 2.32 pts. of suberic acid in solution. (Wirz.)

B. Suberic acid dissolves without decomposition in warm nitric acid. (Chevreul.)

C. With Bases. — The suberates when heated give off their acid partly decomposed, partly undecomposed; the suberic acid is precipitated as a white powder from their solutions on addition of a stronger acid.

*Suberate of Ammonia.* — Crystallises when its solution is slowly evaporated, in slender, white, four-sided needles, of silky lustre, united in tufts. The salt has a pungent saline taste (Brandes); it volatilises when heated, and is readily soluble in water. (Bouillon.) Yields suberamic acid when submitted to dry distillation. (Gerhardt.)

*Suberate of Potash.* — Four-sided prisms (Bouillon); confused crystalline mass, resembling cauliflower-heads; has a neutral reaction and saline taste. (Brandes.) Melts when heated, the acid volatilising. Dissolves with difficulty in water (Bouillon); dissolves readily and becomes moist on exposure to the air. (Brandes.)

*Suberate of Soda* is obtained as a solid, dense white mass, when the acid is saturated with carbonate of soda, and the solution evaporated to dryness. (Bromeis.) White, transparent, rectangular prisms and needles. Neutral. The salt has a bitter saline taste. Dissolves in 1 pt. of cold

and in a smaller quantity of hot water; becomes rather moist by exposure to the air. (Brandes.) Dissolves in alcohol. (Bouillon.)

				Brandes.	Bromeis.
2 NaO .....	62	...	28.44	24.26	28.39
C <sup>16</sup> H <sup>12</sup> O <sup>6</sup> .....	156	...	71.56	75.74	71.61
<hr/>					
C <sup>16</sup> Na <sup>2</sup> H <sup>12</sup> O <sup>8</sup> ....	218	...	100.00	100.00	100.00

*Suberate of Baryta.* — Suberic acid does not cause turbidity in baryta water (Chevreul), but on evaporation, the salt separates as a white powder and in uncrystallised films. Fusible when heated. (Bouillon.) Suberate of ammonia does not precipitate chloride of barium until alcohol is added (Bromeis); the precipitate is at first almost transparent. (Laurent.) The salt is almost tasteless. It dissolves in 59 pts. of cold, and in 16.5 pts. of boiling water. (Brandes.)

				Brandes.
2 BaO .....	153.2	...	49.54	43.58
C <sup>16</sup> H <sup>12</sup> O <sup>6</sup> .....	156	...	50.46	56.42
<hr/>				
C <sup>16</sup> Ba <sup>2</sup> H <sup>12</sup> O <sup>8</sup> .....	309.2	...	100.00	100.00

*Suberate of Strontia.* — Suberic acid does not precipitate strontia water. (Chevreul.) On evaporation, the salt is obtained in slightly transparent films, which give off water in the air and become opaque, melt when heated, and dissolve in 21 pts. of water at 20°, in 12.7 pts. at 30°, in 13.3 pts. at 50° and in 12.8 pts. of boiling water. (Brandes.) Suberate of ammonia does not precipitate chloride of strontium until alcohol is added. (Bromeis.) The precipitate is almost transparent at first. (Laurent.)

				Brandes.
2 SrO .....	103.6	...	39.90	34.52
C <sup>16</sup> H <sup>12</sup> O <sup>6</sup> .....	156	...	60.10	65.48
<hr/>				
C <sup>16</sup> Sr <sup>2</sup> H <sup>12</sup> O <sup>8</sup> .....	259.6	...	100.00	100.00

*Suberate of Lime* is precipitated when the aqueous solution of the salt is evaporated, or when concentrated solutions of suberate of ammonia and chloride of calcium are mixed together (Chevreul); the salt is not precipitated until alcohol is added. (Bromeis.) It has a very weak saline taste. When heated it becomes yellow, then slightly fluid, and burns with intumescence. Soluble in 39 pts. of cold and in 9 pts. of boiling water. (Brandes.)

				Dried at 100°.	Brandes.
2 CaO .....	56	...	26.41	22.67	
C <sup>16</sup> H <sup>12</sup> O <sup>6</sup> .....	156	...	73.59	77.33	
<hr/>					
C <sup>16</sup> Ca <sup>2</sup> H <sup>12</sup> O <sup>8</sup> .....	212	...	100.00	100.00	

*Suberate of Magnesia.* — When suberate of ammonia is mixed with chloride of magnesium and alcohol added, a precipitate is formed, which is at first almost transparent. (Laurent.) White powder and uncrystalline films, tasting first soapy and then rather bitter. Swells up when heated.

Soluble in 1 pt. of water at  $12^\circ$ , and in a smaller quantity of hot water. (Brandes, Bouillon.)

				Brandes.	
2 MgO .....	40	....	20.41	.....	17.53
$C^{16}H^{12}O^8$ .....	156	....	79.59	.....	82.47
<hr/>					
$C^{16}Mg^2H^{12}O^8$ .....	196	....	100.00	.....	100.00

*Suberate of Alumina.* — The ammonia-salt precipitates a saturated solution of alum. (Chevreul.) Not crystallisable. Tastes astringent. (Bouillon.)

*Uranic Suberate.* — Suberate of ammonia forms a bright yellow precipitate with uranic sulphate. The precipitate becomes yellowish white on drying, and contains 58.32 p. c. oxide and 41.68 p. c. of acid; blackens when heated, and evolves white vapours together with a stinking oil, leaving a greenish grey residue of partly reduced oxide. Dissolves in 300 pts. of boiling water. (Brandes.)

*Manganous Suberate.* — Yellowish white, slightly transparent mass resembling cauliflowers. Has a sweetish saline taste with astringent after-taste. Soluble in water. (Brandes.)

*Suberate of Zinc.* — According to Bouillon, zinc-salts are precipitated by free suberic acid; according to Chevreul and Bromeis, only by suberate of ammonia. Soft, white, tasteless powder, which when heated turns yellow, melts, and leaves a residue of oxide of zinc and metallic zinc. (Brandes.)

*Stannous Suberate.* — Suberic acid produces a white precipitate with stannous chloride. (Chevreul.) Suberate of ammonia produces with neutral salts of tin, a white precipitate soluble in alcohol. (Bromeis.)

*Suberate of Lead. — a. Neutral.* — Aqueous suberic acid precipitates acetate and nitrate of lead. (Bouillon, Chevreul, Bromeis.) The salt produced by adding tribasic acetate of lead to aqueous suberic acid as long as a precipitate is produced, contains, after being washed and dried, 58.48 per cent. of oxide to 41.52 per cent. acid. (Bussy.) A solution of acetate of lead is precipitated by suberate of ammonia (Bouillon, Chevreul, Bromeis), by suberate of baryta (Bouillon), or suberate of potash. (Brandes.) Dense white, curdy flakes, which dry up to a white slightly sweet powder. When heated, it melts, swells up, burns, and chars. Nearly insoluble in water. (Brandes.) The salt is completely insoluble in water and in alcohol, even when warm. (Bromeis.) Dissolves in dilute acetic acid. (Bouillon.)

At $100^\circ$ .				Brandes.	Bromeis.
16 C .....	96	....	25.29	.....	25.80
12 H .....	12	....	3.16	.....	3.26
6 O .....	48	....	12.64	.....	13.46
2 PbO .....	223.6	....	58.91	.....	57.63
<hr/>					
$C^{16}Pb^2H^{12}O^8$ ....	379.6	....	100.00	.....	100.00

Brandes found in a former analysis 52.89 per cent. of oxide of lead, Bouillon 71.19 per cent.

*b. Tribasic.* — Obtained by digesting *a* for a long time with basic acetate of lead. (Bromeis.)

					Bromeis.
16 C	.....	96	...	11.61	..... 11.90
12 H	.....	12	...	1.45	..... 1.48
6 O	.....	48	...	5.81	..... 6.21
6 PbO	.....	670.8	...	81.13	..... 80.41
<hr/> $C^{16}Pb^3H^{12}O^8, 4PbO$					..... 826.8 ... 100.00 ..... 100.00

*Ferrous Suberate.* — Suberic acid and suberate of ammonia produce a white precipitate with ferrous sulphate. (Chevreul.) The precipitate melts when heated, and is decomposed with intumescence. It is converted into ferric salt by exposure to the air, and is insoluble in water. (Brandes.)

*Ferric Suberate.* — Suberate of ammonia produces a reddish brown precipitate with ferric hydrochlorate (sulphate). (Bromeis.) The precipitate becomes brown on drying, and melts and swells up when heated. Insoluble in water. (Brandes.)

*Suberate of Cobalt.* — Salts of cobalt form a rose-coloured precipitate with suberate of ammonia. (Chevreul.)

*Suberate of Copper.* — Suberic acid precipitates sulphate, but not nitrate of copper. (Bouillon.) The ammonia-salt, but not the free acid, precipitates copper-salts pale-blue (Chevreul), pale-bluish green (Brandes), of a fine blue-green. (Bromeis.) The salt melts and decomposes when heated. It dissolves very slightly in water. (Brandes.)

					Brandes.
2 CuO	.....	79.6	...	38.79	..... 38.75
$C^{16}H^{12}O^8$	.....	156	...	66.21	..... 71.25
<hr/> $C^{16}Cu^2H^{12}O^8$					.... 235.6 ... 100.00 ..... 100.00

*Mercurous Suberate.* — Suberic acid produces a white precipitate with mercurous nitrate. (Bouillon, Chevreul.) — Aqueous suberic acid dissolves but a small quantity of mercurous oxide. (Harff.) The salt is prepared by precipitating mercurous nitrate with suberate of potash. — White, loosely coherent, tasteless powder. Turns grey when exposed in the moist state to the sun. Contains 70.91 per cent. of mercurous oxide ( $C^{16}H^{12}O^8, 2Hg^2O$  requires 72.72 per cent. of mercurous oxide). A small portion sublimes undecomposed when heated, and leaves a residue of charcoal. With ammonia the salt forms a black double salt; with potash it yields mercurous oxide. Cold nitric acid dissolves the salt slowly, hot nitric acid quickly. By boiling with water or alcohol it is resolved into mercury and the mercuric salt. Insoluble in water. Soluble in 2500 pts. of ether. (Harff.)

*Mercuric Suberate.* — Suberic acid does not dissolve mercuric oxide. — The salt is obtained by precipitating mercuric nitrate with suberate of potash. — White, tasteless powder, which coheres on drying. Contains 56.75 per cent. of oxide ( $C^{16}H^{12}O^8, 2HgO$  requires 58.06 per cent. of oxide). The salt is destroyed by ignition and leaves a residue of charcoal. With ammonia it forms a white double salt; with potash, it yields yellow mercurous oxide. Dissolves in hydrochloric acid and in nitric acid. Requires for

solution more than 2000 pts of cold water; boiling water dissolves it more readily. Nearly insoluble in alcohol, soluble in 1200 pts. of ether. (Harff.)

*Basic Ammonio-mercurous Suberate.* — The mercurous salt is suspended in water and treated with ammonia. Black, light, tasteless powder, containing 85.75 p. c. of mercurous oxide. Evolves ammonia when treated with potash. Hot sulphuric acid destroys the suberic acid and forms a white powder. Dissolves in concentrated acetic acid and leaves metallic globules. Insoluble in water, alcohol, and ether. (Harff.)

*Basic Ammonio-mercuric Suberate.* — Prepared like the mercurous compound. White, tasteless powder, which becomes yellow in the sun. Contains 75.49 p. c. of oxide. Leaves charcoal when ignited. Cold sulphuric acid has no marked action upon the salt; hot sulphuric acid chars the suberic acid and leaves a white powder. Soluble in hydrochloric acid; partially in nitric acid, leaving a white powder. Insoluble in water, alcohol, and ether. (Harff.)

*Suberate of Silver.* — Suberic acid produces a white precipitate with nitrate of silver. (Bouillon, Chevreul.) Suberate of ammonia (and of potash) forms a white precipitate with nitrate of silver. (Brandes, Bromeis.) Pulverulent. (Brandes, Wirz.) Becomes violet on exposure to light (Bussy), especially in the moist state. When heated it melts, turns yellow, and then black, throws out suffocating vapours, and leaves metallic silver. Nearly insoluble in water. (Brandes.)

<i>Dried at 100°.</i>				Bromeis. (Average.)	Wirz.	
2 AgO .....	232	...	59.79	.....	58.02	
16 C .....	96	...	24.74	.....	26.56	... 25.2
12 H .....	12	...	3.09	.....	3.49	... 3.3
6 O .....	48	...	12.38	.....	11.93	
<hr/> $C^{16}Ag^3H^{12}O^8$ .....				388	...	100.00
				.....	100.00	

Bussy found 55.58 p. c. Ag, Wirz, 55.51 p. c. (calculated, 55.67 p. c.).

Suberic acid dissolves in *alcohol*, especially in warm alcohol, in *ether*, and in *oils* both *volatile* and *fatty*. The alcoholic solution is partly precipitated by water. (Chevreul.)

### Suberate of Methyl.



LAURENT. *Ann. Chim. Phys.* 66, 162.

#### *Subérate de Méthylène, Korkformester.*

Prepared in the ordinary way from 2 pts. of suberic acid, 1 pt. of sulphuric acid, and 4 pts. of wood-spirit. The product is purified in the same manner as the ethyl-compound.



Suberate of methyl possesses properties similar to those of the ethyl-compound. Sp. gr. = 1.014 at 18°.

					Laurent.
20 C	.....	120	...	59.41	..... 59.16
18 H	.....	18	...	8.91	..... 9.20
8 O	.....	64	...	31.68	..... 31.64
<hr/>					
$C^{20}H^{18}O^8$	.....	202	...	100.00	..... 100.00

Forms suberamide with ammonia.

### Suberate of Ethyl.



BOUSSINGAULT. *J. pr. Chem.* 7, 211; *Ann. Pharm.* 19, 307.

LAURENT. *Ann. Chim. Phys.* 66, 160.

BROMEIS. *Ann. Pharm.* 35, 101.

*Suberic ether, Subérate d'éthérène, Korknaphtha, Korkvinester.*

**Preparation.** 4 pts. of alcohol are heated with 1 pt. of hydrochloric acid and 2 pts. of suberic acid. (Boussingault.) — 2. Two pts. of suberic acid are boiled with 1 pt. of sulphuric acid and 4 pts. of alcohol, and the ether, which remains in the retort, is washed first with water, then with aqueous potash, dried over chloride of calcium, and distilled. (Laurent.) — 3. Alcoholic suberic acid is saturated with hydrochloric acid gas, whereupon the ether separates out; it is then shaken up with water and dried over chloride of calcium. (Bromeis.)

**Properties.** Thin, limpid liquid (Laurent); oily liquid. (Boussingault.) Has a very faint odour (Laurent, Boussingault); an agreeable odour of apples. (Bromeis.) Has a repulsive taste (Boussingault), like that of rancid hazel-nut-oil. (Laurent.) Boils without decomposition at 230° (Boussingault), at about 260°. (Laurent.) Slightly heavier than water. (Boussingault.) Sp. gr. = 1.003 at 15°. (Laurent.)

					Boussingault.	Laurent.	Bromeis.
24 C	.....	144	...	62.60	..... 62.7	..... 63.05	..... 62.60
22 H	.....	22	...	9.57	..... 9.6	..... 9.77	..... 9.77
8 O	.....	64	...	27.83	..... 27.7	..... 27.18	..... 27.63
<hr/>							
$C^{24}H^{20}O^8$	.....	230	...	100.00	..... 100.0	..... 100.00	..... 100.00

1. Suberate of ethyl does not appear to be decomposed by cold *nitric acid*; hot *nitric acid* decomposes it readily, suberic acid crystallising out on cooling. — 2. Cold *sulphuric acid* dissolves the ether; on heating the solution, decomposition takes place, since water no longer precipitates the ether, and suberic acid crystallises out on cooling. — 3. Aqueous *potash* scarcely attacks the ether, but it is rapidly decomposed by alcoholic potash; and on adding an acid to the solution, nothing but suberic



acid is precipitated. — 4. When treated with *chlorine*, it forms chlorosuberate of ethyl. — 5. Alcoholic *ammonia* converts it into suberamide. (Laurent.)

Suberate of ethyl dissolves in every proportion in *alcohol* and in *ether*. (Laurent.)

### Chlorosuberate of Ethyl.



LAURENT. *Ann. Chim. Phys.* 66, 161.

When a stream of chlorine is passed through cold suberate of ethyl, it acts very slowly upon the ether, and after 12 hours scarcely one-fourth of an atom of hydrogen is replaced. If, however, the treatment is continued and the ether heated, chlorosuberate of ethyl is formed. This is probably not the ultimate product of the action of chlorine.

						Laurent.
24 C	.....	144	....	48.13	.....	48.3
20 H	.....	20	....	6.78	.....	7.2
2 Cl	.....	70.8	....	23.68	} .....	44.5
8 O	.....	64	....	21.41		
<hr/>						
$C^{24}Cl^2H^{20}O^8$	.....	298.8	....	100.00	.....	100.00

### Oxygen-nucleus $C^{16}H^{12}O^4$ .

#### Aloisol.



E. ROBIQUET. *N. J. Pharm.* 10, 241; *J. pr. Chem.* 39, 180; abstr. *N. Ann. Chim. Phys.* 20, 487.

*Formation.* By distilling aloes with lime.

*Preparation.* A finely powdered mixture of 100 grammes of aloes and 50 grammes of lime (if larger quantities are used, secondary products of decomposition may be formed) is gently heated in a retort until white vapours and inflammable gases begin to be evolved. The retort is then removed from the fire, and the reaction continues violently by itself; white vapours and a large quantity of inflammable gases are evolved, and yellow oily drops, consisting of almost pure aloisol, condense in the cool receiver. More aloisol passes over after the evolution of gas has ceased, and the remainder is obtained by heating more strongly, and ultimately to a red heat (or until a reddish oil, containing but little aloisol, distils). As only a small quantity of aloisol is obtained, the distillation must be several times repeated with fresh aloes. The various products are mixed together in a stoppered bottle and set aside, whereby

two strata are formed, the upper consisting of impure and very acid aloisol, and the lower of acid opalescent water (sometimes a few drops of a greenish yellow fixed oil are formed beneath the two strata.) The upper stratum is removed with a pipette, shaken with baryta-water till the acid reaction is destroyed, dried for several days over chloride of calcium in a sealed tube (to prevent absorption of oxygen) and distilled 2 or 3 times in an oil-bath. Only that portion of the oil which passes over at  $130^{\circ}$  is collected and preserved in a sealed tube. 100 pts. of aloes yield 1 pt. of aloisol.

**Properties.** Colourless or pale amber-yellow oil. Sp. gr. = 0.877 at  $15^{\circ}$ . Does not solidify at  $-20^{\circ}$ . Boils at  $130^{\circ}$ . Has a strong penetrating odour, both of potato-oil and oil of bitter almonds.

				Robiquet.	
16 C .....	96	...	61.54	.....	60.42 to 61.54
12 H .....	12	...	7.69	.....	7.26 „ 7.68
6 O .....	48	...	30.77	.....	32.32 „ 30.78
<hr/>					
$C^{16}H^{12}O^6$ .....	156	...	100.00	.....	100.00 100.00

**Decompositions.** Aloisol attracts *oxygen* from the air with avidity, even when poured from one vessel into another, turning red or reddish brown and being converted into aloisic acid.

2. When alcoholic aloisol is heated with *ammonia* and *nitrate of silver*, a metallic mirror is deposited on the sides of the vessel.

3. When 2 or 3 grammes of aloisol are slowly added to a solution of 10 grammes of *chromic acid* in 30 grammes of water, and the whole is warmed, vapours of water are evolved together with carbonic acid gas and a decided odour of oil of bitter almonds, and a milky, neutral, strongly smelling distillate is obtained. When shaken with ether, the distillate immediately becomes clear, and the ether takes up an oil which remains behind on evaporation, and is converted into benzoic acid on exposure to the air for a few days.

4. When aloisol is heated to  $200^{\circ}$  with *oxide of copper*, the same products are formed as by the action of chromic acid:



5. Dilute *nitric acid* also converts aloisol into oil of bitter almonds.

6. Concentrated *nitric acid* converts aloisol, with explosion, into a thick, pitchy oil, which consists almost entirely of aloisic acid, but is soon further oxidised to a mixture of oxalic acid crystals, picric acid, and a red resin possessing a strong odour of bitter almond-oil. No benzoic acid can be detected amongst the products.

7. *Chlorine-water* converts aloisol into aloisic acid. At the same time, a slight odour of bitter almond-oil is produced, but no other product is formed.

**Combinations.** Aloisol is insoluble in *water*.

When dissolved in ether, it absorbs dry ammonia-gas at  $-20^{\circ}$ , and forms an oil, which gives off the ammonia between  $1^{\circ}$  and  $2^{\circ}$ , and dissolves in alcohol, but not in ether or in water. Aloisol mixes in all proportions with *alcohol* and with *ether*.

**Aloisic Acid.**

E. ROBIQUET. *N. J. Pharm.* 10, 246; *J. pr. Chem.* 39, 186.

*Formation.* Formed in the oxidation of aloisol by air, chlorine-water or concentrated nitric acid (p. 215).

It may be freed from aloisol by heat.

Reddish-brown oil, much heavier than water. Smells strongly like castoreum. Boils in the anhydrous state at  $250^\circ$ , but is not volatile.

It becomes rapidly resinized in the air, whence no correct analysis could be made of it. (It appears in every way to be an impure product. Gm.)

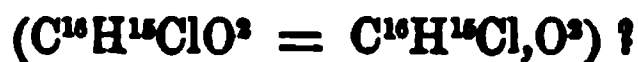
*Bromine-nucleus*  $C^{16}BrH^{16}$ .**Hydrobromate of Bromocaprylene.**

CAHOURS. *Compt. rend.* 31, 143.

BOUIS. *N. Ann. Chim. Phys.* 44, 118.

1. When caprylene, prepared by the method given at page 180, is treated with bromine, it becomes hot and forms a heavy liquid,  $C^{16}Br^3H^{16}$ . (Cahours.)

2. Bromine acts violently upon caprylene, forming a thick colourless liquid. (Bouis.)

*Chlorine-nucleus*  $C^{16}ClH^{16}$ .**Binoxide of Chlorocaprylene.**

CAHOURS. *Compt. rend.* 39, 257; *Pharm. Centr.* 1854, 659.

*Chloride of Capryl.*

This compound mixed with carbolic acid forms hydrochloric acid and a volatile liquid, which, when boiled with potash, is resolved into carbolic acid and caprylic acid.

*Chlorine-nucleus*  $C^{16}Cl^5H^{11}$ .**Pentachlorocaprylene.**

BOUIS.

*Preparation.* When a stream of chlorine is slowly passed into caprylene which is kept cool, the gas is absorbed with evolution of heat,

and the hydrochloric acid is afterwards evolved. As soon as the liquid ceases to absorb gas, even in sunshine, the product is washed and dried.

*Properties.* Thick, viscid liquid.

					Bouis.
16 C	.....	96	...	33.80	..... 33.9
5 Cl	.....	177	...	62.32	..... 62.0
11 H	.....	11	...	3.88	..... 4.0
<hr/>					
$C^{16}Cl^5H^{11}$	.....	284	...	100.00	..... 99.9

Burns with difficulty, and with a smoky flame.

*Nitro-nucleus*  $C^{16}XH^{15}$ .

**Nitrocaprylene.**

$C^{16}NH^{15}O^4 = C^{16}XH^{15}$ .

Bouis. *N. Ann. Chim. Phys.* 44, 118.

*Formation.* 1. By treating caprylene with nitric acid (p. 181).  
2. By distilling binitrocaprylene.

*Preparation.* Binitrocaprylene is submitted to distillation, and when the boiling point of the liquid has risen from  $100^\circ$  to  $200^\circ$ , the retort is taken from the fire, whereupon the temperature still rises as high as  $212^\circ$ , and almost all the liquid passes over, with evolution of red vapours. There remains in the retort a black residue which is heavier than water, dissolves in potash, and is reprecipitated by nitric acid.

*Properties.* Liquid, having a strong, suffocating, disagreeable odour when heated to the boiling point. Lighter than water.

					Bouis.
16 C	.....	96	...	61.14	..... 59.66
N	.....	14	...	8.91	
15 H	.....	15	...	9.55	..... 9.32
4 O	.....	32	...	20.40	
<hr/>					
$C^{16}XH^{15}$	.....	157	...	100.00	

Nitrocaprylene is turned red by potash, and dissolves if the potash-solution is strong. It dissolves in alcohol.

**Nitrocaprylic Acid.**

$C^{16}NH^{15}O^8 = C^{16}XH^{15},O^4$ .

WIRZ. *Ann. Pharm.* 104, 289.

Laurent and Bromeis had previously remarked the thick oil which is formed, together with the bibasic acids, when fatty acids are oxidised by nitric acid.

The heavy viscid oil obtained by treating the fatty acids from cocoa-

nut-oil in the manner described at page 206, is repeatedly washed with hot water, till the grains of suberic acid, which were at first mixed with it, are completely removed. Thus prepared, nitrocaprylic acid still contains nitrocapric acid, from which it cannot be separated.

Yellowish red oil, of the consistence of syrup. Sp. gr. = 1.093 at 18°. Tastes strongly bitter, and has a peculiar smell.

					Wirz.
16 C	.....	96	...	50.7	..... 49.13
N	.....	14	...	7.4	..... 8.86
15 H	.....	15	...	7.9	..... 7.67
8 O	.....	64	...	34.0	..... 34.34
<hr/>					
$C^{16}XH^{15}O^4$	.....	189	...	100.0	..... 100.00

When heated, nitrocaprylic acid soon assumes a dark colour, evolves vapours which excite coughing, together with an odour of nitrous acid, explodes slightly, and burns completely away.

Very slightly soluble in *water*. Soluble in concentrated *nitric acid*.

Neutralises *ammonia* and *potash* completely; forms with ammonia a yellowish red solution; with potash, a deep red solution, which, when evaporated, leaves a thick uncrystallisable mass becoming brown in the air. Nitrocaprylate of ammonia is precipitated in flakes by salts of *lime*, *baryta*, *lead*, and *copper*; on stirring the liquid, the flakes cohere into a viscid mass like plaster.

*Nitrocaprylate of Silver*. — Nitrate of silver precipitates from a solution of nitrocaprylate of ammonia, yellowish white flakes, which rapidly become brownish red on exposure to the air, and dry up to a light, yellowish grey mass.

					Wirz.
16 C	.....	96	...	82.4	..... 30.46
N	.....	14	...	4.7	..... 6.80
14 H	.....	14	...	4.7	..... 4.70
Ag	.....	108	...	36.4	..... 35.73
8 O	.....	64	...	21.8	..... 22.31
<hr/>					
$C^{16}XH^{14}AgO^4$	.....	296	...	100.0	..... 100.00

Nitrocaprylate of silver from other preparations, was found to possess a different composition, because it contained nitrocapric acid.

### Nitrocaprylate of Ethyl.



WIRZ. *Ann. Pharm.* 104, 290.

Obtained by passing hydrochloric acid gas into an alcoholic solution of nitrocaprylic acid, and purified from adhering acid by washing with dilute carbonate of soda and then with water. The product is freed from water by drying over sulphuric acid.

Yellow oil, more mobile than nitrocaprylic acid. Sp. gr. = 1.031 at 18°. Has a pleasant, fruity odour.

					Wirz.
20 C .....	120	...	55.3	.....	55.4
N .....	14	...	6.4		
19 H .....	19	...	8.7	.....	8.9
O .....	64	...	29.6		
<hr/>					
$C^{20}H^{38}O^4$ .....	217	...	100.0		

*Nitro-nucleus*  $C^{16}X^2H^{14}$ .

**Binetrocaprylene.**



BOUIS. *loc. cit.*

*Formation.* By treating caprylene with nitric acid (p. 181) or with fuming nitric acid and oil of vitriol.

*Preparation.* Caprylene is first treated with quadrihydrated nitric acid, then with a mixture of fuming nitric acid and oil of vitriol, which induces a violent action, continuing in the cold. The oily liquid is washed and dried.

*Properties.* Liquid, heavier than water; its aqueous solution has a violently irritating odour.

					Bouis.
16 C .....	96	...	47.52	.....	48.05
2 N .....	28	...	13.83		
14 H .....	14	...	6.93	.....	7.40
8 O .....	64	...	31.72		
<hr/>					
$C^{16}N^2H^{14}O^8$ ....	202	...	100.00		

*Decompositions.* When distilled it decomposes, with evolution of red vapours, into nitrocaprylene and a black residue (p. 217).

It is but slightly soluble in water, imparting to it a yellow colour.

*Amidogen-nucleus*  $C^{16}AdH^{15}$ .

**Caprylamine.**



W. S. SQUIRE. *Chem. Soc. Qu. J.* 7, 108; *Pharm. Centr.* 1855, 256; *Ann. Pharm.* 92, 400.

CAHOURS. *Compt. rend.* 39, 254; *Ann. Pharm.* 92, 399.

BOUIS. *N. Ann. Chim. Phys.* 44, 139.

*Capryliaque, Capryliak, Caprylamin.*

*Formation.* 1. By heating iodide of capryl with alcoholic ammonia (Squire, Cahours, Bouis.)

2. By distilling sulphocaprylate of potash with cyanate of potash, a fluid distillate is obtained which readily crystallises. It consists of probably cyanate and cyanurate of capryl, and when treated with potash yields caprylamine. (Bouis.)

*Preparation.* Iodide of capryl is heated with aqueous ammonia in a sealed tube for two days to  $100^{\circ}$ . The liquid is evaporated almost to dryness, the residue distilled with potash, and the distillate dehydrated by solid potash. (Squire.)

2. An alcoholic solution of iodide of capryl is saturated with dry ammoniacal gas, and the mixture is transferred to a glass tube, which is sealed, and heated in the water-bath. For some hours the iodide floats on the surface, but gradually disappears if the heat is continued. If the contents remain clear on cooling, the ammonia and alcohol are evaporated, and the residual crystalline easily soluble mass is decomposed by caustic potash. (If an oily layer remains floating on the surface, not disappearing by repeated treatment with alcoholic ammonia, and seems to contain bi- and ter-caprylamine, it must be removed with a pipette.) Impure caprylamine then collects on the surface, as a brown, strongly odorous liquid, which is purified by decantation, washing and distillation, either alone or over fragments of potash. (Bouis.)

*Properties.* Clear, colourless liquid. Tastes bitter. (Squire.) Odour ammoniacal (Cahours); fishy (Squire); strongly persistent and goat-like. (Bouis.) Boils at  $164^{\circ}$  (Squire); at  $172^{\circ}$  —  $175^{\circ}$  (Cahours); at  $175^{\circ}$ . (Bouis.) Sp. gr. 0.786. (Squire.) It is strongly caustic. (Bouis.)

					Squire.
16 C .....	96	....	74.42	.....	74.29
19 H .....	19	....	14.73	.....	14.61
N .....	14	....	10.85	.....	11.10
<hr/>					
$C^{16}H^{19}N$ .....	129	....	100.00	.....	100.00

*Decompositions.* Caprylamine burns readily. (Bouis.) By the action of iodide of capryl, it gives further substituted ammonias. With the chlorides of benzoyl and cuminyll, it forms compounds corresponding to benzamide and cuminamide. (Cahours.)

*Combinations.* Caprylamine does not dissolve in water. Like ammonia, it precipitates metallic salts and dissolves chloride of silver. (Bouis.)

Caprylamine combines readily with acids to form salts. (Cahours, Bouis.)

*Sulphate of Caprylamine.* —  $C^{16}H^{19}N,HO,SO^3$  is crystalline and easily soluble in water. (Cahours.)

*Hydriodate of Caprylamine.* —  $C^{16}H^{19}N,HI$ , is obtained by heating iodide of capryl with alcoholic ammonia. Forms large plates. Dissolves easily in hot water. (Cahours.)

*Hydrochlorate of Caprylamine.* —  $C^{16}H^{19}N,HCl$ . — Caprylamine in presence of hydrochloric acid, forms thick white fumes. (Bouis.) It combines energetically with hydrochloric acid to form a very deliquescent

salt, the solution of which, evaporated in vacuo, is at first sticky, but afterwards forms large plates having a mother-of-pearl lustre. (Bouis, Cahours.)

*Nitrate of Caprylamine.* —  $C^{16}H^{19}N, HO, NO^3$ . — Crystallisable, and readily soluble in water. (Cahours.)

*Gold-salt.* —  $C^{16}H^{19}N, HCl, AuCl^3$ . — The concentrated solution of hydrochlorate of caprylamine solidifies with terchloride of gold. From dilute solutions, brilliant yellow laminæ separate, resembling iodide of lead.

Changes when exposed to light in the moist state. Melts under  $100^\circ$  to a red liquid, and when more strongly heated, takes fire and burns with a beautiful flame, leaving a residue of gold. Deliquescent. Dissolves in *alcohol* and *ether*. (Bouis.)

*Platinum-salt.* — Hydrochlorate of caprylamine gives with bichloride of platinum, a yellow crystalline (amorphous, Bouis) precipitate, which as the boiling aqueous solution cools, is obtained in lustrous, golden-yellow scales. (Cahours.)

Large, thin plates, containing 29.41 p. c. platinum, and 28.37 p. c. carbon. ( $C^{16}H^{19}N, HCl, PtCl^2 = 29.5$  p. c. platinum, and 28.6 p. c. carbon). (Squire.)

The salt melts when heated, leaving as residue a black, combustible substance mixed with platinum. (Bouis.) It is but slightly soluble in cold, but more soluble in hot water. It dissolves readily in alcohol and in ether.

*Oxyamidogen-nucleus*  $C^{16}AdH^{12}O^2$ .

**Suberamic Acid.**

$C^{16}NH^{15}O^4 = C^{16}AdH^{12}O^2, O^2$ .

GERHARDT. *Compt. Chim.* 1845, 178.

*Suberaminsäure, Acide suberamique.*

In the destructive distillation of suberate of ammonia, water and ammonia first pass over, and then suberamic acid.

Fusible, soluble in boiling water, from which it is deposited on cooling.

When the acid is boiled with carbonate of baryta, the filtrate gives, with nitrate of silver, a gelatinous precipitate resembling alumina and containing 38 p. c. silver. ( $C^{16}NAgH^{14}O^2$  requires 38.57 p. c. silver.)

*Oxyamidogen-nucleus*  $C^{16}Ad^2H^{12}O^2$ .

**Suberamide.**

$C^{16}N^2H^{16}O^4 = C^{16}Ad^2H^{12}O^2, O^2$ .

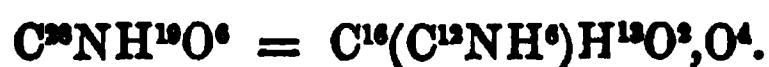
LAURENT. *Rev. scient.* 10, 123; *J. pr. Chem.* 27, 313.

Suberate of methyl in presence of aqueous ammonia changes after some days to a white crystalline substance. — Suberate of ethyl is not



changed by aqueous ammonia; but if ammoniacal gas be passed through the alcoholic solution of this compound, a small precipitate, like the above, is formed. This suberamide is washed with a little cold alcohol, then crystallised from hot alcohol.

### Suberanilic Acid.



LAURENT and GERHARDT. *N. Ann. Chim. Phys.* 24, 185.

*Suberanilsäure, Acide suberanilique.*

**Preparation** (see *Suberanilide*.) When the alcoholic liquid from which suberanilide is precipitated by water, is evaporated till the alcohol is driven off, a brownish oil separates, which solidifies on cooling. This oil is dissolved in boiling ammonia, which leaves a certain quantity of suberanilide, and filtered; from the filtrate hydrochloric acid precipitates colourless suberanilic acid. If during the boiling, a slight excess of hydrochloric acid be added, suberanilic acid separates on cooling, partly crystalline and partly as a pale yellowish oil which afterwards solidifies.

Microscopic laminæ, irregularly notched. Melts at  $128^{\circ}$ , becoming crystalline on cooling. The solution in hot water reddens litmus.

	<i>Fused.</i>			Laurent & Gerhardt.	
28 C .....	168	...	67.47	.....	67.5
N .....	14	...	5.62		
19 H .....	19	...	7.63	.....	7.8
6 O .....	48	...	19.28		
<hr/>					
$C^{28}NH^{19}O^6$ .....	249	...	100.00		

**Decompositions.** The acid subjected to destructive distillation yields much charcoal and a thick oil containing aniline, which partly solidifies on cooling; this substance is soluble in a small quantity of ether, with the exception of a white powder which is abundantly soluble in boiling alcohol or ether, and crystallises out on cooling; fused with potash it gives off aniline, and is not dissolved by aqueous potash or ammonia; hence it is probably suberanilide. — 2. Suberanilic acid yields aniline when fused with potash.

Suberanilic acid is not soluble in cold, and but slightly soluble in hot water.

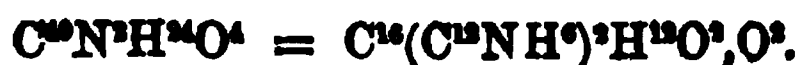
**Suberanilate of Ammonia.** — The acid dissolves easily in hot ammonia, and the salt is deposited in small granular crystals, whose aqueous solution is not coloured by chloride of lime.

The ammonia-salt precipitates *chloride of barium*; the precipitate dissolves readily in boiling water, and separates on cooling in woolly flakes. With *chloride of calcium*, it gives a white precipitate soluble in hot water; with *lead-salts*, a white precipitate insoluble in water. It precipitates *ferrous-salts* yellowish-white, *cupric-salts* light blue; the precipitate is insoluble in water.

*Suberanilate of Silver.* — White precipitate insoluble in water, and containing 30·2 p. c. silver. (Calculated  $C^{18}H^{18}AgNO^6 = 30·36$  p. c. Ag). Assumes a violet colour in the light.

Suberanilic acid dissolves readily in ether and crystallises by spontaneous evaporation in small needles.

### Suberanilide.



LAURENT & GERHARDT. *N. Ann. Chim. Phys.* 24, 184.

When equal measures of dry aniline and fused suberic acid are melted together, water is produced. The mixture is kept melted for ten minutes near the boiling heat; and an equal bulk of alcohol is then added, which immediately dissolves the mixture. After a few minutes the solution solidifies to a mass of crystals, which are dissolved in more boiling alcohol, and the solution is left to stand, whereupon most of the suberanilide crystallises out. The rest is precipitated by water, the suberanilic acid remaining in solution.

Crystallises from alcohol in pearly laminæ. Melts at  $183^\circ$ , and crystallises on cooling.

					Laurent & Gerhardt.	
40 C	.....	240	...	74·07	.....	73·7
2 N	.....	28	...	8·64		
24 H	.....	24	...	7·41	.....	7·5
4 O	.....	32	...	9·88		
<hr/>						
$C^{18}N^2H^{24}O^4$	.....	324	...	100·00		

Therefore neutral suberate of aniline minus  $4HO$ . (Laurent and Gerhardt.)

When subjected to destructive distillation, it leaves a small quantity of charcoal, and yields an oil, which solidifies on cooling, and crystallises from a hot alcoholic solution on cooling, in pearly laminæ, which however present a different appearance under the microscope, and seem to be somewhat rounded.

Gently heated with hydrate of potash, it immediately gives off aniline. It is not attacked by ammonia or by boiling solution of potash.

It is but slightly soluble in cold alcohol, but dissolves readily in boiling alcohol and in ether.

*Oxyazo-nucleus*  $C^{18}N^4H^8O^4$ .

### Caffeine.



CHEVREUX. *Tulloch. Phil. Mag.* 12, 350; *Scher. J.* 10, 108.

HERMANN. *Crell. Ann.* 1800, 2, 108 and 176; *N. Gehl.* 6, 522.

- CADET. *Ann. Chim.* 58, 266; *N. Gehl.* 6, 535.  
 PAYSSÉ. *Ann. Chim.* 59, 196 and 293; *N. Gehl.* 6, 525.  
 SCHRADER. *N. Gehl.* 6, 544.  
 SEGUIN. *Ann. Chim.* 92, 5; *N. Tr.* 1, 2, 98.  
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 STENHOUSE. *Phil. Mag. J.* 23, 426; *Mem. Chem. Soc.* 1, 215 and 237; *Ann. Pharm.* 45, 366; 46, 227; *Phil. Mag. J.* 42, 21; *J. pr. Chem.* 61, 351; *Ann. Pharm.* 89, 244; *Ann. Pharm.* 102, 124.  
 PELIGOT. *N. Ann. Chim. Phys.* 11, 138.  
 ROCHLEDER. *Ann. Pharm.* 50, 231; 63, 201; *Wien. Akad. Ber.* 1849, 96; *Ann. Pharm.* 69, 120; 71, 1; *Wien. Akad. Ber.* 1850, 296; *J. pr. Chem.* 51, 401.  
 E. C. NICHOLSON. *Chem. Soc. Qu. J.* 3, 321; *Phil. Mag. J.* 31, 115; *Ann. Pharm.* 62, 71; *J. pr. Chem.* 41, 457.  
 BÖDECKER. *Ann. Pharm.* 71, 63.  
 PAYEN. *Compt. rend.* 23, 9; *N. Ann. Chim. Phys.* 26, 109.  
 HEIYNSIUS. *J. pr. Chem.* 49, 317.  
 VERSMANN. *N. Br. Arch.* 68, 148.  
 HINTERBERGER. *Ann. Pharm.* 82, 311.  
 KOHL & SWOBODA. *Ann. Pharm.* 83, 341; *Pharm. Centralbl.* 1852, 953.  
 STENHOUSE, GRAHAM, & CAMPBELL. *Chem. Soc. Qu. J.* 9, 33; *Pharm. Centralbl.* 1857, 53.  
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 A. VOGEL, junr. *Kunst. u. Gewerbebl. für Bayern.* 1858, 27; *Chem. Centralbl.* 1858, 367.

*Coffein, Caffeeestoff, Caffeebitter, Cafëine, Théine, Thein, Guaranin.*

In 1821 the bitter principle of coffee, which had hitherto been known only in the impure state, was first prepared in the pure crystallised form by Pelletier and Caventou, Robiquet and Runge. In 1838, Mulder and C. Tobst discovered simultaneously, that theine, discovered by Oudry in 1827, is identical with caffeine, as Berzelius had already suggested. In 1840, the guaranine of Th. Martius was recognised, both by its discoverer and by Berthemot and Dechastelus, as likewise identical with caffeine.

**Sources.** In the fruit (and the leaves, according to Van Den Corput and Stenhouse) of the coffee plant. In tea. (Oudry.) In guarana, the dried paste of the fruit of *Paulinia sorbilis*. (Th. Martius.) In Paraguay-tea, the leaves and twigs of *Ilex paraguayensis* (Stenhouse), always combined with tannic acid. (Compare Rochleder, *Ann. Pharm.* 76, 10.) According to Payen, it is combined in coffee with chlorogenic acid, as chlorogenate of caffeine and potash.

Guarana contains 5.07 p. c.; good black tea from Kemaon in the East Indies, 1.97 p. c.; various kinds of coffee, 0.8 — 1 p. c.; coffee-leaves from Sumatra, 1.26; Paraguay-tea, 1.2 p. c. of caffeine. (Stenhouse.)

To detect caffeine in mixtures which contain about 10 p. c. of coffee, the infusion is evaporated with lime, the dry residue exhausted with ether, and the residue remaining after the evaporation of the ether is treated with nitric acid and ammonia (p. 230). (Stenhouse, Graham, and Campbell.)

**Preparation.** — I. *From Coffee.* — 1. Robiquet digests the cold aqueous extract of raw coffee with magnesia, evaporates the filtrate, and purifies the caffeine which crystallises out, by solution in water or alcohol and crystallisation. (A mucous substance contained in the coffee materially hinders the preparation.)

2. The alcoholic extract of raw coffee is exhausted with water; the aqueous solution separated from the fat is heated with magnesia; the precipitate is well washed; the filtrate evaporated to dryness; the extract boiled six times with absolute alcohol, which takes up all the caffeine, and only a trace of colouring matter, gum and sugar; and the alcoholic tincture is filtered through purified animal charcoal, distilled, and allowed to cool. The caffeine then crystallises out beautifully. (Pelletier.)

3. The cold aqueous extract of the beans is first precipitated with neutral acetate of lead, then with basic acetate; the filtrate treated with sulphuretted hydrogen, filtered, and evaporated; the crystalline residue extracted with warm alcohol; and the solution evaporated. (Runge.) Garot, who uses the decoction of the beans, omits the precipitation with basic acetate; neutralises with ammonia the acetic acid set free after precipitation with sulphuretted hydrogen; and lastly evaporates, cools and purifies by recrystallisation the crystals thus obtained. Roasted coffee also yields caffeine, but in smaller quantity.

Pfaff neutralises with carbonate of potash, the evaporated liquid remaining after precipitation with sulphuretted hydrogen; filters from the precipitated carbonate of lime, and from the carbonate of magnesia which separates out on concentration; boils with bone-charcoal; evaporates to crystallisation; and finally decolorises and purifies the crystals thus obtained: the mother-liquor yields a further quantity, by recrystallisation from alcohol of 76 p. c. The product is 0.2 p. c. of caffeine. — E. Polacci (*Cimento*. 5, 396) exhausts the coffee by repeated boiling with water, precipitates the united aqueous extracts with neutral acetate of lead, removes the lead by sulphuretted hydrogen, and evaporates the filtrate to the crystallising point. The product thus obtained from Martinique coffee amounted to about 0.5 per cent.

4. Coffee, slightly roasted, is powdered (it is more easily pulverised than raw coffee), and boiled twice with four parts of water; the infusions are filtered or strained and neutralised with a few drops of caustic soda; and a concentrated decoction of gall-nuts is added. A bulky, caseous precipitate then forms, which rapidly subsides (if it remains suspended, dilute caustic soda or sulphuric acid is added according to the state of the liquid), and is thrown upon a thick cloth and pressed out. The precipitate

is triturated with a quantity of quick-lime equal in weight to 10 p. c. of the coffee, and twice boiled with alcohol of  $33^\circ$ ; the solution is filtered; the alcohol distilled off; the residue evaporated to crystallisation; and the resulting crystals, which are somewhat greenish, are purified by recrystallisation. From various kinds of coffee, 0.4 to 0.9 p. c. of caffeine are obtained. (Robiquet and Boutron.)

5. Stenhouse repeatedly boils the pulverised beans with water; precipitates while still hot with basic acetate of lead; boils the filtrate with hydrated oxide of lead; filters; evaporates to dryness; heats the residue, mixed with sand, in a Mohr's subliming apparatus; and purifies the sublimed caffeine by repeated sublimation at a gentle heat. The product amounts to 0.2 p. c. Zenneck obtained from raw coffee 0.75; from roasted, 0.42 p. c. caffeine, by extracting it with water, evaporating the solution, treating the residue with alcohol, evaporating the alcoholic solution, and subliming this extract mixed with pounded glass.

6. The pulverised raw beans are extracted with aqueous ether; the ether is distilled off; the residual butyry extract repeatedly shaken with one-fifth of its volume of water; and the water removed with a syphon. The aqueous solution is freed from acids by basic acetate of lead, filtered, treated with sulphuretted hydrogen, and again filtered and evaporated to a syrup, whereupon, after some time, caffeine crystallises out in white needles. Ether extracts all the caffeine from coffee. (Rochleder.) In this operation, Payen uses the ether-extracting apparatus (*N. J. Pharm.* 13, 59); boils out with water; evaporates the solution to dryness; extracts the residue with absolute alcohol; and again evaporates. A crystalline residue then remains, which, after washing with cold alcohol, is dissolved in hot alcohol, and several times recrystallised therefrom.

7. Hydrate of lime prepared from 2 parts of caustic lime is mixed with 10 parts of ground coffee; the mixture is extracted in the displacement apparatus with alcohol of  $80^\circ$  (Richter), as long as the filtrate leaves any caffeine on evaporation; the residue in the apparatus is dried and pulverised (which is easier, and more complete than with fresh coffee) and again extracted with alcohol, which takes out all the caffeine. From both these spirituous solutions, the alcohol is expelled by distillation; water is added to the residue; the oil which separates out on repose is removed; and the liquid is evaporated, till it solidifies in the cold to a mass of crystals. These are pressed from the mother-liquor (which furnishes an additional quantity of caffeine on evaporation) and adhering oil, and recrystallised from water with addition of animal-charcoal. Brazilian coffee thus treated yields 0.57 per cent. (Versmann.)

8. The pulverised coffee-beans are digested for a week with commercial benzol, which takes up caffeine and oil of coffee. Both remain, on distilling off the benzol, and are separated by hot water, which dissolves the caffeine, and yields it in large crystals on evaporation. From the mixture of caffeine and oil of coffee, the latter may be extracted by ether, which leaves the caffeine behind. (Vogel.)

II. *From Tea.*—(Green tea contains the largest proportion of theine.) — 1. One part of tea is extracted with 8 parts of water to which one-third of salt has been added; the filtrate is evaporated to dryness; the residue exhausted with alcohol of  $40^\circ$  B, filtered, and evaporated to a syrup; and the residue is dissolved in hot water and filtered hot: the filtrate on cooling deposits a bitterish resin. The filtered liquid is boiled with magnesia, then filtered and evaporated till it crystallises. (Oudry.)

(According to Oudry, the magnesia residue contains theine; on the other hand, Günther and Mulder obtained little or none.) There remains at last a crystallisable extract, from which, by extraction with ether, a considerable quantity of theine may be obtained, so that the total yield is about 0.5 p. c. The extraction with alcohol may be omitted; the salt-infusion, or tea-infusion, or simply tea and water may be boiled with magnesia; and the filtered liquid evaporated to an extract, and exhausted with ether without waiting for the crystallisation, which is difficult to produce (Mulder). Or since ether does not easily dissolve the theine enclosed in foreign substances, Peligot first extracts with alcohol the aqueous infusion of tea, after evaporation to dryness with magnesia (whereby however ammonia and ammoniacal-salt are formed from a part of the theine); evaporates to dryness; and exhausts the residue with ether. 2.2 to 4.4 p. c. of theine are thus obtained. (Peligot.) According to Oudry, the solution boiled with magnesia and filtered, yields on evaporation an extract which is rich in tannin, but does not yield any pure theine by extraction with alcohol and evaporation to the crystallising point, even when this operation is repeated. The impure product is therefore dissolved in water; the remainder of the tannin precipitated by basic acetate of lead; the lead precipitated by sulphuretted hydrogen; and the filtrate evaporated: pale yellowish theine then crystallises out, and is purified by repeated treatment with alcohol. (Günther.)

2. Coarsely pulverised tea is macerated with 78 p. c. alcohol for 48 hours, and strained; the residue is treated three times with 2 parts of alcohol for 24 hours, and pressed; the tincture is precipitated with basic acetate of lead; the filtrate separated by sulphuretted hydrogen from excess of lead, then filtered and evaporated in a retort to one-fourth; and the residue is neutralised with potash and evaporated till it crystallises. One pound of tea gives 1 dram of pure theine. (Herzog.) Instead of neutralising with potash, Günther boils with excess of magnesia; or he evaporates a tea-decoction made with 85 p. c. alcohol to a soft extract; boils this with water; sets it aside 24 hours, whereupon the resin, enclosing all the theine, separates; decants the water; dissolves the resin in alcohol; precipitates with basic acetate of lead, and then the filtrate with sulphuretted hydrogen; and evaporates to the crystallising point. Much of the theine remains dissolved in the acetic acid. (Herzog.) Jobst boils tea or tea-dust repeatedly with water; precipitates with basic acetate of lead; leaves the solution to crystallise; and treats the mother-liquor either with animal-charcoal, or once more with basic acetate of lead. Stenhouse precipitates the alcoholic extract of tea with excess of acetate of lead; evaporates to dryness; and obtains the theine by sublimation. He obtained about 1 p. c. of theine. Peligot mixes infusion of tea, precipitated by basic acetate of lead, with ammonia; boils for some time; filters; passes sulphuretted hydrogen through the liquid; and again filters and crystallises.

3. Waste, useless tea is gradually heated in Mohr's sublimation-apparatus, but not so far as to induce the decomposition of the theine. Part of the sublimate is quite pure — the remainder is purified by recrystallisation from water. (Heiynsius.)

III. *From Guarana.* — 1. Guarana mixed with three-tenths of burnt lime is repeatedly boiled with alcohol of 33° Beck; the filtrate evaporated a little; the greenish fatty oil which separates on cooling is separated; the residual alcoholic liquid completely evaporated; and the



dry residue heated: caffeine then sublimes, at first yellowish white, and afterwards quite white. (Martius.)

2. Pulverised guarana is exhausted with boiling alcohol; the liquid filtered; the alcohol distilled off; and water added, which separates a greenish oil; this is removed, and the liquid evaporated to dryness. (Berthemot and Dechastelus.)

3. Twenty-four grammes of guarana powder are boiled with a quart of water; the cold solution is precipitated with basic acetate of lead; the bulky brownish red precipitate filtered off, and repeatedly digested with hot water; and the lead is separated from the filtrate by sulphuretted hydrogen. The liquid separated from the sulphide of lead is evaporated in the water-bath to dryness; the residue dissolved in a little boiling alcohol, filtered, and allowed to crystallise; and the crystals thus obtained are purified by pressing and recrystallisation. (Stenhouse.)

IV. *From Paraguay-tea.*—The filtered decoction is precipitated with neutral acetate, and the filtrate with basic acetate (or it is boiled with litharge), and the liquid decanted from the precipitate is evaporated to dryness, a tough, dark brown, hygroscopic mass then remaining. From this residue, caffeine may be obtained, either by sublimation, or by reducing it to powder, mixing it with sand, and treating it with ether. After distilling off the ether, feebly coloured caffeine crystallises, and may be purified by repeated crystallisation. The product amounts to 0.13 p. c. of the Paraguay-tea. (Stenhouse.)

*Properties.* Crystallises from a concentrated aqueous solution in white, silky, opaque, flexible needles; from a dilute solution, in long, transparent needles having but little flexibility (Pelletier); colourless, transparent, silky needles like asbestos (Robiquet, Giese); delicate, feathery prisms. (Oudry.) The long colourless needles become transparent when dried. Caffeine crystallises from water, when not quite pure, in needles united in groups; from alcohol by spontaneous evaporation, in arborescent needles; from very dilute alcohol, in fine silky needles. (Günther.) From the extract prepared according to Oudry's method, it crystallises in white, lustrous, hexagonal, pointed, very hard prisms; from the aqueous solution, in needles, which cannot be made to assume the peculiar form of those which crystallise from the extract. (Mulder.) Very light. (Berthemot and Dechastelus.) Heavier than water. (Mulder.) Sp. gr. 1.23 at 19°. (Pfaff.) Grates when bitten between the teeth. (Mulder.) Inodorous even when sublimed. (Pfaff.) Tasteless. Tastes feebly bitter (Giese, Robiquet, Pfaff, Herzog); especially in acid or alcoholic solution. (Buchner.) Neutral. (Robiquet, Günther, Pfaff, Jobst.) Feebly alkaline. (Martius.) Permanent in the air. (Pfaff, Herzog.) Becomes opaque when heated. (Nicholson.) Melts at a temperature above 100° (Zenneck); at 177.8° (Mulder), forming a transparent liquid, and sublimes completely at 184.7° (Mulder), without decomposition, in hair-like, partly feathery needles, resembling benzoic acid. (Robiquet, Zenneck, Martius.) Boils at 384°. (Peligot.)—Half a grain exhibited poisonous action on rabbits. (Mulder.) For physiological action of caffeine, compare J. Lehmann, *Ann. Pharm.* 87, 205 and 207.

					Dumas & Pelletier.	Pfaff & Liebig.
16 C	.....	96	...	49.48	..... 46.51	.... 49.31
4 N	.....	56	...	28.86	..... 21.54	.... 29.03
10 H	.....	10	...	5.16	..... 4.81	.... 5.33
4 O	.....	82	...	16.51	..... 27.14	.... 16.33
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C <sup>16</sup> N <sup>4</sup> H <sup>10</sup> O <sup>4</sup>	.....	194	...	100.00	..... 100.00	.... 100.00

		Wöhler.		Jobst.		Berthémot & Dechastelus.		Martius.
16 C	.....	49.25	...	49.42	...	49.62	...	49.10
4 N	.....	28.97	...	29.01	...		...	29.18
10 H	.....	5.43	...	5.21	...	5.57	...	5.14
4 O	.....	16.35	...	16.36	...		...	16.58
<hr/>								
$C^{16}N^4H^{10}O^4$	.....	100.00	...	100.00	...		...	100.00

	Mulder.		Stenhouse.		Nicholson.
			<i>a.</i>	<i>b.</i>	
16 C .....	49·48	....	49·04	....	49·09
4 N .....	28·52	....	28·78	....	28·81
10 H .....	5·37	....	5·14	....	5·16
4 O .....	16·63	....	17·04	....	16·94
<hr/>					
C <sup>16</sup> H <sup>4</sup> H <sup>10</sup> O <sup>4</sup> .....	100·00	....	100·00	....	100·00

Dumas & Pelletier, Pfaff & Liebig examined caffeine prepared from coffee; Jobst, Mulder and Stenhouse (a) that from tea; Berthémot, Dechastelus and Martius that from guarana; Stenhouse (b) that from Paraguay-tea. Payen found in caffeine from tea, 50.86 C, 30.00 N, and 5.08 H, and proposed the formula  $C^{16}N^4H^{10}O^3$ .

**Decompositions.** 1. Caffeine melts, when heated in a platinum spoon, giving off white feebly aromatic vapours (peculiar penetrating vapours (Martius), like methylamine (Rochelder); and forms on cooling a resinous transparent mass; at a stronger heat, it turns grey, becomes crystalline after cooling, and yields a grey powder; at a still higher temperature, it swells up and volatilises completely, without leaving any carbonaceous residue. Heated in a glass tube, it melts to a yellow liquid, gives off water, and then sublimes in white vapours, which do not turn turmeric brown, and condense to fine needles. (Günther.) By dry distillation, especially with addition of potash, it gives off ammonia. (Martius.)

2. Melts when quickly heated in the air, and burns with a blue flame, leaving little or no charcoal. (Herzog, Mulder.)

3. Caffeine does not pass into putrid fermentation.

4. It is but slightly decomposed when evaporated with phosphoric acid. (Zenneck.)

5. Heated with *oil of vitriol*, it gives off acid (empyreumatic, Zenneck) vapours, partly volatilises, and is partially carbonised. (Martius.) Oil of vitriol decomposes it only after continued heating. (Jobst, Mulder.)

6. With iodine it forms a brown mass. (Martius.)

7. It is not changed by dry chlorine. (Mulder.) — When chlorine is passed through a thick paste of caffeine and water, the mixture becomes heated to 50°, the caffeine disappears, and chlorocaffeine (with a com-



paratively small quantity of chlorine), amalic acid (xi, 433), nitrotheine (x, 453), and methylamine are formed. The resulting liquid heated in the water-bath gives off chlorine, hydrochloric acid, and a body smelling like chloride of cyanogen, and granular crystals of amalic acid separate, succeeded, if too much chlorine has not been passed through the liquid, by chlorocaffeine in light flakes and crusts. The liquid filtered from this deposit and further evaporated in the water-bath, continually gives off hydrochloric acid, and leaves a reddish yellow syrup which solidifies on cooling. This syrup strained through linen yields a colourless crystalline mass of nitrotheine, and a yellow syrup of hydrochlorate of methylamine ;



8. When caffeine is boiled with hydrochloric acid and chlorate of potash, and the solution cautiously evaporated, a crystalline mass remains, which is either alloxan or a similar body; when dissolved in water, it colours the skin red, and imparts to it a peculiar odour. The solution mixed with alkalis and ferrous salts acquires the colour of indigo, and forms with ammonia a solution of murexide. (Rochleder.)

9. Nitric acid dissolves caffeine, and decomposes it after continued heating. (Jobst.) Boiled with fuming nitric acid for a few minutes, caffeine evolves nitrous fumes, and yields a dark yellow solution, which when gently evaporated to dryness, leaves a dark yellow mass, and when gently heated with a drop of ammonia, produces a colour like that of purpurate of ammonia. This red substance dissolves in water and in alcohol with a carmine-red colour; but not in ether. Potash destroys the colour, without producing indigo-blue. This reaction serves for the detection of caffeine. The yellow solution gently evaporated to a syrup, yields long hard, colourless needles, which, when purified by crystallisation, are but little coloured by ammonia. When the boiling with a large excess of nitric acid is continued for some hours, till a drop of the solution leaves on evaporation, not a yellow, but a white residue, these needles also disappear, ammonia no longer produces a characteristic colour, and on evaporation to a syrup, and cooling, laminæ of nitrotheine are obtained, together with a mother-liquor which contains abundance of deliquescent ammonia-salts. (Stenhouse.) Nitric acid acts like moist chlorine, forming products varying with the concentration, the temperature, and the duration of the action. The substance here produced, which assumes with ammonia the colour of murexide, is also produced by aqua regia, by chlorine, and by chlorate of potash and hydrochloric acid. (Rochleder.) Nitric acid does not produce from caffeine either picric acid (Pfaff) or oxalic acid. (Mulder.)

10. Caffeine yields by boiling with *polysulphide of ammonium*, a solution which exhibits an evanescent sulphocyanogen reaction with sesquichloride of iron. (Rochleder.)

11. Boiled with very strong *caustic potash*, it evolves a considerable quantity of methylamine. (Wirz.) According to earlier statements, it gives off ammonia by boiling or fusing with potash.

12. With soda-lime at  $180^\circ$ , it gives off ammonia, forms carbonate of soda, carbonate of lime and a large quantity of cyanide of sodium. Piperine, morphine, quinine and cinchonine thus treated do not yield cyanide of sodium. (Rochleder.) With lime, caffeine does not evolve ammonia. (Martius.)

**Combinations. With Water.** — *a. Hydrated Caffeine.* — Caffeine crystallised from water contains water of crystallisation (Pfaff and Liebig, Jobst, Martius); but not when crystallised from ether (Mulder). From water also small anhydrous needles are obtained; when crystals deposited from ether are immersed in a concentrated aqueous solution, hydrated crystals are afterwards deposited in other parts. (Mulder.)

					Liebig & Pfaff.		Mulder.		Martius.
$C^{16}N^4H^{10}O^4$ .....	194	...	91.51	...	92.15	...	91.51	...	91.86
2 Aq .....	18	...	8.49	...	7.85	...	8.49	...	8.14
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$C^{16}N^4H^{10}O^4 + 2Aq$ ....	212	...	100.00	...	100.00	...	100.00	...	100.00

The crystals give off their water at 100° (Pfaff and Liebig, Martius); not completely till they are heated to a temperature above 120° (Mulder); and become dull and friable. (Pfaff and Liebig).

*b. Aqueous Caffeine.* — Caffeine dissolves sparingly in cold, easily in hot water. 1 part of caffeine dried at 120° dissolves at 12.5 in 98 parts water; 1 part crystallised caffeine in 93 parts. (Mulder.) It dissolves in 35 to 40 parts of cold water (Oudry), in 48 parts at 21° (Zenneck), in 50 parts (Pfaff), in 100 parts at 15° (Günther).

The aqueous solution of caffeine is not altered by boracic, phosphoric, sulphuric, hydrochloric or nitric acids, by ammonia (Mulder), by the fixed alkalis, either pure or carbonated (Herzog, Mulder), by iodide of sodium (Mulder), by baryta- or lime-water (Pfaff, Mulder), by chromate of potash (Mulder), by metallic-salts (Pfaff, Herzog), by protochloride of tin (Nicholson), bichloride of tin, neutral or basic acetate of lead, sesquichloride of iron, acetate (Mulder), or sulphate of copper, mercurous sulphate (Nicholson), chloride of mercury, alcoholic solution of bichloride of platinum, ferrocyanide of potassium (Mulder), or tartar emetic (Pfaff). It does not precipitate a solution of gelatin. (Pfaff.)

**With Acids.** — Caffeine combines with strong acids to form salts having an acid reaction. (Herzog.) The salts which Giese, Pelletier & Caventou, and Oudry thought they had obtained, appear to have been pure caffeine.

It dissolves quickly in acids (slowly in oxalic and in tartaric acid, Mulder); the solutions are acid. They are not precipitated by potash. (Jobst.) On evaporating solutions of caffeine in acidulated water, caffeine free from acid crystallises out. (Pelletier, Mulder.)

Caffeine dissolves rapidly in aqueous boracic, and phosphoric acids, but on evaporation caffeine free from acid is obtained. (Mulder.)

**Sulphate of Caffeine.** — Asbestos-like needles. (Oudry.) Caffeine forms with sulphuric acid, an acid and a neutral salt, which dissolve more easily in water than in alcohol. (Günther.) Dilute sulphuric acid rapidly dissolves caffeine, but no solid sulphate is obtained. (Mulder.) Concentrated sulphuric acid dissolves caffeine without decomposition, and forms on evaporation, a salt which crystallises slowly in silky needles, has an acid and rather bitter taste, and is sparingly soluble in ether. (Herzog.)

Caffeine crystallises unchanged from dilute perchloric acid. (Boedeker, *Ann. Pharm.* 71, 63.)

*Hydrochlorate of Caffeine.* — Caffeine dissolves easily in hydrochloric acid. (Günther.) *a. Normal.* — Caffeine dissolves in concentrated hydrochloric acid (on the addition of water or of alcohol a considerable quantity of hydrate of caffeine crystallises out). The solution, concentrated by gentle evaporation, is left to crystallise, and the crystals obtained are washed with ether. (Herzog.)

Beautiful large crystals (Herzog) belonging to the oblique prismatic system, partly resembling crystals of sphene, and partly those of epidote. The length of the principal axis is subordinate, that of the second lateral axis is more prominent, the faces are regularly arranged about the semi-axes (but, do they belong to the oblique prismatic system? Gm.)  $n : n = 118\frac{1}{2}^\circ$ . The acute terminal planes are inclined to the lateral edges at an angle of  $116\frac{1}{2}^\circ$ . (Blasius.) The crystals readily give off hydrochloric acid in the air, and effloresce; but even after passing dry hot air for six hours over them, a certain portion of the hydrochloric acid remains. (Herzog.)

				Herzog.
$C^8N^4H^{10}O^4$ .....	194	...	84.21	86.02
HCl .....	36.4	...	15.79	13.98
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$C^8N^4H^{10}O^4, HCl$ ....	230.4	...	100.00	100.00

*b. Acid.* — 100 parts of anhydrous caffeine absorb 32.82 parts when dry hydrochloric acid gas is passed over it. If air be afterwards passed over, hydrochloric acid is expelled. Caffeine saturated with hydrochloric acid forms with water, an acid solution from which caffeine crystallises. (Mulder.)

				Mulder.
$C^8N^4H^{10}O^4$ .....	194	...	72.72	75.29
2 HCl .....	72.8	...	27.28	24.71
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$C^8N^4H^{10}O^4, 2HCl$ ....	266.8	...	100.00	100.00

*Nitrate of Caffeine.* — Caffeine dissolves easily in nitric acid, (without decomposition, even in the concentrated acid: Herzog), and the colourless solution yields a neutral salt having the form of caffeine (Günther); a crystallisable, acid and bitter salt, very sparingly soluble in ether. (Herzog.) Pfaff and Mulder were not able to prepare a nitrate of caffeine.

Caffeine dissolves more easily in ammonia and in potash than in water. The solutions are colourless. (Pfaff.)

Phosphomolybdic acid dissolved in nitric acid forms with solution of caffeine a bright yellow, voluminous precipitate, which behaves with reagents like the precipitate obtained by phosphomolybdic acid in solution of conine. (Sonnenschein.)

Boiled with sesquichloride of iron, caffeine yields on cooling a reddish brown precipitate, which dissolves completely in water, and is probably a double salt. (Nicholson.)

*Nitrate of Silver with Caffeine.*—1. Nitrate of silver in excess is poured into an aqueous or alcoholic solution of caffeine. If both solutions are concentrated, the compound separates in white crystalline hemispheres which adhere firmly to the glass vessel. (Nicholson.) — 2. Caffeine dissolved in water together with nitrate of silver, and evaporated, forms a white

crystalline compound which contains nitric acid, oxide of silver and caffeine, and detonates when heated, giving off red vapours. (Rochleder.) In the dry state, it does not blacken in the light, but becomes violet-coloured when moist. When more strongly heated, it decomposes with volatilisation of caffeine (1 Gm.) and leaves a residue of silver. Dissolves with difficulty in cold, more readily in hot water or in alcohol. (Nicholson.)

					Nicholson.
16 C .....	96	...	26.37	.....	26.45
5 N .....	70	...	19.23		
10 H .....	10	...	2.74	.....	2.86
10 O .....	80	...	22.00		
Ag.....	108	...	29.66	.....	29.79
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$C^{16}N^4H^{10}O^4, AgNO^6$ .....	364	...	100.00		

*Ohloride of Mercury with Caffeine.* — Aqueous or alcoholic solution of caffeine is mixed with excess of corrosive sublimate. The mixture, at first clear, solidifies in a few minutes into a mass consisting of small, white needles. These are purified by recrystallisation from water or alcohol. (Nicholson.) An alcoholic solution of caffeine containing hydrochloric acid, gives with corrosive sublimate the same needles, which may be gently heated till solution takes place, and washed after recrystallisation, with water, alcohol and ether. (Hinterberger.)

Needles resembling caffeine, but smaller. (Nicholson.) Long, silky needles, partially grouped in stars. (Hinterberger.) They dissolve in water, hydrochloric acid, alcohol and oxalic acid, with which latter substance they appear to form a crystalline compound. Nearly insoluble in ether. May be dried at  $100^\circ$  without decomposition, and without loss. (Nicholson.)

				At $100^\circ$ .			Nicholson. Hinterberger.		
16 C .....	96	...	20.65	.....	20.30	...	20.45		
4 N .....	56	...	12.08						
10 H .....	10	...	2.15	.....	2.32	...	2.14		
4 O .....	32	...	6.88						
2 Hg.....	200	...	43.00	.....	42.91	...	42.61		
2 Cl .....	70.8	...	15.24						
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$C^{16}N^4H^{10}O^4, 2HgCl$ .....	464.8	...	100.00						

*Chloroaurate of Caffeine.* — Solution of chloride of gold is added in excess to a solution of caffeine in hydrochloric acid. In concentrated solutions the mixture quickly solidifies to a mass of splendid lemon-yellow crystals. The crystals are washed with cold water, recrystallised from alcohol, and dried in the water-bath.

The compound when crystallised from alcohol, forms long orange-coloured needles having a strong metallic taste. When dry, it does not change in the light or at  $100^\circ$ . The aqueous solution, kept for some time in a state of ebullition, deposits yellow flakes, which do not dissolve in water or alcohol, but are soluble in hydrochloric acid. If the solution is kept for some hours at  $68^\circ$ , gold separates from it in lustrous laminæ. (Nicholson.)

				Nicholson,
16 C .....	96	....	17.98	17.72
4 N .....	56	....	10.50	
11 H .....	11	....	2.06	2.11
4 O .....	32	....	6.01	
Au .....	196.66	....	36.85	37.02
4 Cl .....	142	....	26.60	
<hr/>				
$C^{16}N^4H^{10}O^4, HCl, AuCl^3$ ....	533.66	....	100.00	

*Chloroplatinate of Caffeine.* — Alcoholic bichloride of platinum does not precipitate the aqueous solution of caffeine. (Mulder.) When bichloride of platinum is added to a hot solution of hydrochlorate of caffeine, the mixture on cooling deposits granular crystals which must be washed with alcohol or ether. (Stenhouse, Nicholson.) Small but very distinct orange-yellow crystals; more permanent than hydrochlorate of caffeine (Stenhouse); they do not lose weight at  $100^\circ$ , or undergo any alteration by exposure to light. (Nicholson.) The platinum-salt of caffeine boiled with nitric acid, dissolves with evolution of red vapours, and the liquid on cooling deposits a new platinum-salt in brilliant hexagonal prisms. (Rochleder.)

Sparingly soluble in water, alcohol and ether. (Nicholson.)

				Stenhouse.	Nicholson.
16 C .....	96	....	23.97	24.22	23.96
4 N .....	56	....	13.98		
11 H .....	11	....	2.74	2.89	2.86
4 O .....	32	....	8.02		
Pt .....	98.9	....	24.70	24.49	24.58
3 Cl .....	106.5	....	26.59		
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$C^{16}N^4H^{10}O^4, HCl, PtCl^2$ ....	400.4	....	100.00		

Rochleder found 24.55 p. c. platinum.

With *chloride of palladium*, hydrochlorate of caffeine forms a beautiful brown precipitate, and the filtrate deposits yellow scales of another compound, not unlike iodide of lead. (Nicholson.)

*Cyanide of Mercury with Caffeine.* — (First observed by Nicholson.) — Obtained by mixing a hot solution of caffeine in 85 p. c. alcohol with a hot aqueous solution of cyanide of mercury. The mixture, at first clear, deposits, on cooling, an abundance of colourless needles, which, after being washed with water and alcohol, do not change at  $100^\circ$ . Prisms belonging to the square prismatic system, but seldom having their terminal faces completely developed  $\bar{P}4. \infty \bar{P}. \infty \bar{P} \infty. a : b : c = 1 : 1.7851 : 0.8281$ . (Schabus.) The salt dissolves, with difficulty, in cold water and alcohol. (Kohl and Swoboda.)

				Kohl & Swoboda.
$C^{16}N^4H^{10}O^4$ .....	246	....	55.16	
2 Hg .....	200	....	44.84	45.11
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$C^{16}N^4H^{10}O^4, 2HgCy$ ....	446	....	100.00	

Caffeine dissolves in 20 parts of alcohol at  $21^\circ$  (Zenneck), in 25 parts

of 85 per cent alcohol, at 20°. (Günther.) Crystallised caffeine dissolves in 158 (?) parts of anhydrous alcohol at 12.50; caffeine dried at 120°, in 97 parts. (Mulder.) It does not dissolve in absolute alcohol. (Pfaff.) It dissolves easily in hot alcohol.

It does not dissolve in ether (Pfaff), very little (Robiquet, Martius, Herzog); in 300 parts. (Peligot.) Crystallised caffeine dissolves in 218 parts of ether; after drying at 120°, in 194 parts (?) at 12.5° (Mulder); readily, with the aid of heat. (Jobst, Mulder.)

Caffeine dissolves easily in acetic acid (Pfaff); slowly in oxalic and tartaric acids, and crystallises from the latter solutions unchanged. (Mulder.) It forms with citric acid (Oudry) a salt crystallising in long thin silky needles; according to Günther, on the contrary, no such salt is produced.

*Tannate of Caffeine.*—The aqueous solution of caffeine forms, with an infusion of galls (no precipitate, according to Pfaff, but according to Herzog and Martius) an abundant white precipitate, which dissolves in alcohol. (Mulder.) Infusion of tea, by its tannin, also gives with solution of caffeine a precipitate which is large or small, according as the tea infusion is strong; pure tannin does the same. The precipitate is dissolved on heating the aqueous liquid. (Mulder.)

To prepare the salt, aqueous caffeine is added in excess to aqueous tannic acid, the precipitate dissolved on the filter in alcohol, and the solution evaporated. It contains 41.9 per cent. caffeine, and 58.1 per cent. tannic acid. (Mulder.)

Caffeine dissolves in volatile, not in fatty oils (Herzog), not in oil of turpentine (Pfaff), but very easily in oil of rosemary. (Günther.) It may be melted with camphor to a slightly crystalline mass. The solution in oil of almonds partly assumes, on cooling, an imperfectly crystalline character, and partly forms an unctuous mass; water and alcohol extract the caffeine from it. (Martius.)



### Chlorocaffeine.



ROCHLEDER. *Wien. Akad. Ber.* 1856, 2, 96; *J. pr. Chem.* 56, 403.

*Formation.* (p. 230.) The product obtained by the imperfect action of chlorine on caffeine suspended in water, is purified by three or four recrystallisations from water. It forms a light bulky mass, and crystallises in needles from alcohol.

*Decomposition.* By the continued action of chlorine, it forms chloride of cyanogen, methylamine, and amalic acid (p. 230.)

*Cyanazo-nucleus*  $C^{16}CyN^3H^{13}$ .**Cyanethine.**FRANKLAND & KOLBE. *Ann. Pharm.* 65, 282; *Chem. Soc. Qu. J.* 1, 60.*Cyanäthin, Kyanäthin.*

**Formation and Preparation.** Cyanide of ethyl is gradually dropped on potassium, and at last gently heated as long as gas ( $C^4H^6$ ) continues to escape. A yellowish tough mass then remains, from which cold water dissolves much cyanide of potassium, leaving a white substance undissolved. This substance is washed with cold water and dissolved in hot water, which, on cooling, deposits pearly crystalline laminæ. The quantity of cyanethine thus obtained amounts to only a small percentage of the cyanide of ethyl; if the potassium be directly added to an excess of cyanide of ethyl, scarcely a trace is obtained. White, inodorous, tasteless. Melts at about  $190^\circ$ , and begins to boil at  $208^\circ$ , but only a portion of it volatilises undecomposed. When dissolved in warm water, it has a feeble but distinct alkaline reaction.

<i>Dried at <math>100^\circ</math>.</i>				Frankland & Kolbe.	
				<i>mean.</i>	
18 C .....	108	...	65.45	.....	65.60
3 N .....	42	...	25.45	.....	25.50
15 H .....	15	...	9.10	.....	9.25
<hr/>					
$C^{18}N^3H^{16}$ .....	165	...	100.00	.....	100.35

Cyanethine may be boiled with *caustic potash* without decomposition; when it is evaporated to dryness with potash, and heated, most of it sublimes unchanged and the residue does not blacken.

It dissolves but very sparingly in cold water, more readily in hot water, and crystallises out on cooling. Dissolves easily in all *acids*. The sulphate and hydrochlorate of cyanethine do not crystallise, and dissolve easily in water.

**Nitrate of Cyanethine.**—The solution of cyanethine in dilute nitric leaves, on spontaneous evaporation, large colourless prisms, which, after recrystallisation, are quite neutral.

<i>Dried at <math>100^\circ</math>.</i>				Frankland & Kolbe.	
18 C .....	108	...	47.4	.....	47.5
4 N .....	56	...	24.6	.....	24.6
16 H .....	16	...	7.0	.....	7.0
6 O .....	48	...	21.0	.....	20.9
<hr/>					
$C^{18}N^3H^{16}, HO, NO^5$ ....	228	...	100.0	.....	100.0

**Chloroplatinate of Cyanethine.**—Concentrated solutions of hydrochlorate of cyanethine and bichloride of platinum form a red crystalline precipitate, which separates from solution in water by spontaneous evaporation in large ruby-red octobedrons.



On boiling the alcoholic solution, protochloride of platinum is formed. Dissolves with difficulty in water, with tolerable facility in alcohol and ether-alcohol.

				Frankland & Kolbe.	
18 C	.....	108	....	29.1	..... 29.1
3 N	.....	42	....	11.4	
16 H	.....	16	....	4.3	..... 4.4
Pt	.....	99	....	26.5	..... 26.2
3 Cl	.....	106.2	....	28.7	
<hr/>					
$C^{18}N^3H^{16}, HCl, PtCl^2$ .....				371.2	.... 100.0

*Acetate of Cyanethine.* — The solution of cyanethine in acetic acid gives off acetic acid on evaporation in vacuo, and leaves a basic insoluble salt.

*Oxalate of Cyanethine.* — Large prisms, formed by the spontaneous evaporation of the base saturated with oxalic acid.

The *terchloromethylsulphite of cyanethine* crystallises.  
Cyanethine dissolves in *alcohol* in almost all proportions.

*Primary Nucleus*  $C^{18}H^{18}$ .

*Oxygen-nucleus*  $C^{18}H^{12}O^6$ .

**Glucic Acid.**



PELIGOT (1838). *Ann. Chim. Phys.* 67, 154.

MULDER. *J. pr. Chem.* 21, 229.

*Glucinsäure, Acide kalisaccharique.*

*Formation.* 1. By the action of the stronger bases, such as potash, soda, baryta, strontia, lime, oxide of lead, on an aqueous solution of cane or grape sugar; slowly at ordinary, more rapidly at higher temperatures. (Peligot.) — 2. Crystallised diabetic sugar treated with oxide of lead, at  $110^\circ$ , gives off 28 per cent. of water and is converted into glucic acid. (Peligot.) — 3. It is also formed, together with ulmin and humin substances, on boiling cane-sugar with sulphuric acid and water.

*Preparations.* 1. A solution of sugar-lime is allowed to stand till the alkaline reaction has completely disappeared and carbonic acid no longer produces a precipitate; a quantity of oxalic acid, exactly sufficient to precipitate the lime, is added, and the whole is evaporated and filtered;— or better: basic acetate of lead is added instead of oxalic acid, by which, a more abundant white precipitate is formed; and this, when washed diffused in water, decomposed with sulphuretted hydrogen, and filtered from the sulphide of lead, yields aqueous glucic acid. (Peligot.)

2. A hot and concentrated solution of hydrate of baryta or lime is



mixed with grape-sugar melted in its water of crystallisation at  $100^{\circ}$ , whereupon violent action is at once set up, heat is evolved, and, by the formation of large quantities of aqueous vapour, a portion of the mass may be scattered about. (When potash or soda is used, this always takes place.) The mass thus obtained consists chiefly of glucic acid, but contains also a brown substance (into which the glucic acid would be entirely changed by continuing the heating), which may be precipitated by the cautious addition of small quantities of basic acetate of lead. (Peligot.)

3. The brownish-red liquid, obtained after long boiling of cane-sugar with sulphuric acid and water, is neutralised with chalk; and after separating the humus substances, the syrup is evaporated with excess of chalk, the residue treated with a little water, the solution filtered, and the brown filtrate evaporated to a syrup, whereupon it again becomes acid. Even by another neutralisation, only a portion of the free acid is removed. This syrup contains—besides a little sulphate of lime—sugar of mucilage, apoglucate of lime and glucate of lime. It is mixed with alcohol, filtered from the abundantly precipitating greyish-brown flakes of apoglucate of lime, and the filtrate, now less deeply coloured, is treated with animal charcoal, which still takes up apoglucate of lime. The decolorised filtrate, when evaporated in vacuo, yields an almost colourless syrup, in which needles of biglucate of lime are formed after a few days. The residual syrup is mixed with small quantities of lime, as long as it remains clear (whereby the acid reaction is almost entirely destroyed), and then mixed with alcohol, which throws down white flakes of monoglucate of lime; these are washed with alcohol in an atmosphere free from carbonic acid, then pressed, and dried at  $100^{\circ}$  over chloride of calcium in vacuo. (Carbonic acid would form carbonate of lime and free glucic acid, which would pass through the filter with the alcohol.) Owing to the presence of a slight excess of glucic acid, the alcoholic wash-water holds in solution glucate of lime and sugar of mucilage; on standing in the air, it deposits carbonate of lime and yields crystals of biglucate of lime. The residual, strongly acid liquid, again saturated with lime, and precipitated with alcohol, yields a further quantity of glucate of lime, and so on till all the glucose is transformed.

The glucate of lime is dissolved in water and precipitated with basic acetate of lead; the white precipitate is washed and decomposed with sulphuretted hydrogen; the liquid filtered, and the filtrate evaporated in vacuo: glucate of lime then remains. (Mulder.)

*Properties.* The acid after drying in vacuo, forms an uncrystallisable, highly hygroscopic mass, resembling tannic acid. (Peligot.) Solid mass which does not attract moisture from the air. (Mulder.) It hardens in the air, even after evaporation to a syrup. (Mulder.) Tastes and reacts strongly acid.

*Decompositions.* 1. Mixed with yeast it does not ferment. (Peligot.) — 2. Heated above  $100^{\circ}$ , it gives off a large quantity of water and turns brown. (Peligot.) — 3. When its aqueous solution is boiled in the air, or with dilute hydrochloric or sulphuric acid, or when the solution of its lime-salt is evaporated in the air, it turns brown and yields apoglucic acid. — 4. By boiling with moderately concentrated sulphuric acid, it is completely changed into humin. (Mulder.)

Dissolves easily in water (Mulder); in all proportions. (Peligot.)

Forms, with bases, neutral salts, which are all soluble in water, with the exception of the lead-salt. (Peligot.) Forms two series of salts, bibasic (neutral) and monobasic (acid). (Mulder.)

*Glucate of Lime. — a. Bibasic. —* Forms a white jelly when pure. The salt, dried in vacuo at 100°, is permanent in the air, but has an amber colour, arising from the presence of apoglucic acid. May be powdered. Smells like paper when burnt. Decomposes by contact with carbonic acid, yielding carbonate of lime and the biacid salt; hence the jelly, when exposed to the air, is changed into a hard mixture of carbonate and biglucate of lime. Dissolves easily in water, sparingly in alcohol. (Mulder.)

Dried in vacuo at 100°.				Mulder.
16 C .....	96	...	88.24	87.97
11 H .....	11	...	4.38	4.46
11 O .....	88	...	35.06	34.48
2 CaO .....	56	...	22.32	23.09
<hr/> C <sup>16</sup> Ca <sup>2</sup> H <sup>10</sup> O <sup>12</sup> + Aq .....				100.00

According to Gerhardt, it is perhaps C<sup>24</sup>Ca<sup>3</sup>H<sup>15</sup>O<sup>18</sup> + Aq. Calculation 38.81 C, 4.03 H, 22.58 CaO. (*Traité* 2, 563.)

*b. Monobasic. —* Carbonate of lime forms with glucic acid, not the neutral, but the acid salt. Dissolves easily in alcohol. The concentrated aqueous solution forms a sticky syrup, which crystallises in needles. (Mulder.)

*Glucate of Lead and Calcium. —* Obtained by precipitating a glucate with basic acetate of lead. White precipitate.

				Peligot.
16 C .....	96	...	14.97	14.35
10 H .....	10	...	1.56	1.97
10 O .....	80	...	12.48	13.43
4 PbO .....	455.2	...	70.99	70.25
<hr/> C <sup>16</sup> Pb <sup>2</sup> H <sup>10</sup> O <sup>12</sup> , 2PbO .....				100.00

According to Gerhardt, it is perhaps C<sup>24</sup>Pb<sup>3</sup>H<sup>15</sup>O<sup>18</sup> + Aq. Calculation requires 15.0 C; 1.7 H; 70.0 PbO.

Bibasic glucate of lime precipitates mercurous nitrate and nitrate of silver. It does not precipitate nitrate of baryta, sesquichloride of iron, or acetate of copper. (Mulder.)

Glucic acid dissolves readily in alcohol. (Mulder.)

*Oxygen-nucleus* C<sup>16</sup>H<sup>10</sup>O<sup>8</sup>.

**Jelly from Pine-needles.**



KAWALIER. *Wien. Akad. Ber.* 11, 344; *Ann. Pharm.* 88, 370.

*Sources.* In the needles and bark of *Pinus sylvestris*. By boiling with feebly alkaline water, pine needles which have been exhausted with

alcohol, a dirty greenish brown decoction is obtained, from which hydrochloric acid precipitates reddish brown gelatinous flakes. These are freed from resin by boiling with alcohol; dissolved in water containing potash, and precipitated with hydrochloric acid, after evaporating the alcohol: the precipitate is then washed with alcohol and dried at  $100^{\circ}$ . — Pine-bark exhausted with alcohol, yields when boiled with alkaline-water, a dark-red decoction; and this precipitated with hydrochloric acid, gives dark red flakes, which are washed with water, then with alcoholic ether and boiling alcohol, dissolved in very dilute aqueous potash, precipitated with hydrochloric acid, washed with alcohol, and dried at  $100^{\circ}$ .

Reddish brown powder, soluble only in alkaline liquids.

				Kawalier.	
				from needles.	from bark.
16 C	96	...	51.61	51.00	51.18
10 H	10	...	5.37	5.46	5.39
10 O	80	...	43.02	43.54	43.43
$C^{16}H^{10}O^{10}$				100.00	100.00

In the analyses, a small quantity of ash has been subtracted.

### Appendix.

#### Jelly from Pine-bark and *Thuja Occidentalis*.



KAWALIER. *Ann. Pharm.* 88, 374; *J. pr. Chem.* 64, 18.

Sources. 1. In the bark of *Pinus sylvestris*. — 2. In the green parts of *Thuja occidentalis*.

Preparation. Like that of the jelly from pine needles.

				Kawalier.
				from Thuja.
At $100^{\circ}$ .				
16 C	96	...	43.64	43.81
12 H	12	...	5.45	5.48
14 O	112	...	50.91	51.21
$C^{16}H^{12}O^{14}$				100.00

				Kawalier.
				from Pinus.
At $100^{\circ}$ .				
16 C	96	...	47.52	47.39
10 H	10	...	4.95	5.09
12 O	96	...	47.53	47.52
$C^{16}H^{10}O^{12}$				100.00

When prepared from *Thuja*, it likewise contained ash, amounting to 5.44 per cent.

When prepared from *Pinus*, its ammoniacal solution gives, with chloride of barium, a flocculent precipitate, which, after drying at 100°, contains 31.93 p. c. carbon, 3.97 hydrogen, and 26.49 baryta, and is, therefore,  $C^{16}H^{12}O^{14},BaO$ . (Calculation requires 32.37 C., 4.04 H., 25.81 BaO.)

*Appendix to Anisene.*

**Anhydrous Anisic Acid.**



PISANI. *Compt. rend.* 44, 837; *J. pr. Chem.* 71, 189.

*Anisic anhydride, Anissäure-anhydrid, Acide anisique anhydre.*

*Formation and Preparation.* 6 atoms of dried and powdered anisate of soda are mixed in a flask with 1 atom of pentachloride of phosphorus; the mass, after the action is terminated, is treated with cold water; the liquid is filtered; and the anhydrous acid remaining on the filter, is washed, pressed between filtering paper, and crystallised from ether.

*Properties.* Concentrically united, silky needles, which melt towards 99° and distil at a higher temperature.

					Pisani.
16 C .....	96	....	67.13	.....	66.95
7 H .....	7	....	4.89	.....	5.17
5 O .....	40	....	27.98	.....	27.88
<hr/>					
$C^{16}H^7O^5$ .....	143	....	100.00	.....	100.00

With boiling water it melts and, after some time, forms anisic acid; with heated potash and ammonia it forms anisates.

Does not dissolve in water, potash, or ammonia. Dissolves readily in alcohol and ether, especially when warm, most easily in a mixture of the two.

**Anisuric Acid.**



CAHOURS. *Compt. rend.* 44, 570; *Pharm. Centr.* 57, 466.

*Anisursäure, Acide anisurique.*

*Formation.* Obtained by the action of chloride of anisyl on silver-glycocol.

Crystallises well.

Heated with acids, it is resolved into glycocol and anisic acid.

Forms crystallisable salts.

**Anisosalicyl.**

CAHOURS. *Compt. rend.* 44, 1254; *Pharm. Centr.* 57, 585.

Produced by the action of chloride of anisyl on salicylous acid, hydrochloric acid being at the same time evolved.

Neutral. Exactly like acetosalicyl.

*Appendix to Vol. xii, p. 246.*

**Acetosalicyl.**

CAHOURS. *Compt. rend.* 44, 1253; *Pharm. Centr.* 1857, 585.

*Formation and Preparation.* Salicylous acid, heated with chloride of acetyl, is briskly attacked, with disengagement of hydrochloric acid and formation of a beautifully crystallising substance.

*Properties.* Perfectly neutral needles. Can be distilled.

						Cahours.		
						<i>a.</i>	<i>b.</i>	
18 C	.....	108	....	65·85	.....	65·82	....	66·05
8 H	.....	8	....	4·78	.....	4·85	....	4·82
6 O	.....	48	....	29·37	.....	29·33	....	29·13
<hr/>								
C <sup>18</sup> H <sup>8</sup> O <sup>6</sup>	.....	164	....	100·00	.....	100·00	....	100·00

*b* was previously distilled at a red heat over anhydrous baryta.

Isomeric with cumaric acid, and with anhydrous acetobenzoic acid.

*Decompositions.* 1. Not altered by aqueous ammonia, by aqueous, alcoholic, or solid potash, or even by anhydrous baryta at a red heat. — 2. It is violently attacked by bromine, chlorine, and fuming nitric acid, forming substitution-products which crystallise well.

*Combinations.* Acetosalicyl does not dissolve in water. It scarcely dissolves in cold, more readily in boiling alcohol, and crystallises in beautiful needles on cooling.

According to Schüller (*J. pr. Chem.* 72, 258), pure chloride of acetyl does not act upon salicylous acid in the cold, but forms when heated with it, a brown unctuous mass which does not yield acetosalicyl. On the other hand, chloride of acetyl containing terchloride of phosphorus, becomes heated in contact with salicylous acid, evolving hydrochloric acid, and, forming as it cools, a crystallisable product which has all the properties of Cahours' acetosalicyl, but contains on the average 73.33 per cent. carbon, and 4.67 per cent. hydrogen; hence Schüller ascribes to it the formula  $\text{C}^{36}\text{H}^{14}\text{O}^8$  (calculation 73.47 p. c. C. and 4.76 p. c. H). The same body is formed, though more slowly, by adding phosphorous acid to

salicylous acid mixed with chloride of acetyl, and separates on evaporation in oily drops which soon change into a crystalline solid, and are obtained pure by washing with water and repeated crystallisation from alcohol. — Brilliant white prisms, often an inch long, which melt at  $130^{\circ}$ , and become solid and crystalline on cooling. They lose scarcely any weight at  $110^{\circ}$ .

This body does not appear to be decomposed by a stronger heat. It is not changed by *potash*, *soda*, or *ammonia*, by dilute *acids*, by *peroxide of lead*, or by *terchloride of phosphorus*. *Oil of vitriol* dissolves the crystals, disengaging the odour of salicylous acid; the solution filtered after saturation with chalk, or carbonate of baryta, colours sesquichloride of iron violet. *Chloride of zinc* at the boiling heat acts like oil of vitriol. *Concentrated nitric acid* forms picric acid; *chromic acid* forms salicylous acid. On boiling with dilute hydrochloric acid and chlorate of potash, there is gradually formed a yellow resin, which smells like chlorokinone, and separates from its solution in boiling alcohol in pale yellow nodules. These crystals are not chloranil; they are not altered by sulphurous acid, ammonia, or potash, and melt into oily drops when heated.

The compound does not dissolve in water, but little in cold alcohol, more abundantly in boiling alcohol. It dissolves in alcoholic potash, whence it is precipitated by water. It dissolves readily in ether. (Schüler.)

## COMPOUNDS CONTAINING 18 AT. CARBON.

*Primary Nucleus*  $C^{18}H^6$ .

*Azo-nucleus*  $C^{18}NH^6$ .

**Chinoline.**

$C^{18}NH^7 = C^{18}NH^6, H^1$ .

RUNGE (1834). *Pogg.* 31, 68.

GERHARDT. *Ann. Pharm.* 42, 310; 44, 279; *J. pr. Chem.* 28, 76; *N. Ann. Chim. Phys.* 7, 252; *Rev. scient.* 10, 186; *Compt. Chim.* 1845, 30.

A. W. HOFMANN. *Ann. Pharm.* 47, 31; *N. Ann. Chim. Phys.* 9, 129; *Ann. Pharm.* 53, 427; 74, 15.

BROMEIS. *Ann. Pharm.* 52, 130.

LAURENT. *N. Ann. Chim. Phys.* 19, 367.

GR. WILLIAMS. *Chem. Gaz.* 1855, 301 and 325; *J. pr. Chem.* 66, 334; *N. Ann. Chim. Phys.* 45, 488; *Chem. Gaz.* 1856, 261 and 281; *J. pr. Chem.* 69, 355.

V. BABO. *J. pr. Chem.* 72, 73.

*Chinolin.* *Leucol* (Runge). *Quinoleine* (Gerhardt).

Discovered by Runge, in 1839, in coal-tar; Gerhardt (1842) obtained it by distilling quinine or cinchonine with hydrate of potash. Runge's

leucol was found, in an elaborate investigation by Hofmann, to be identical with Gerhardt's chinoline. The mixed nature of the chinoline obtained from cinchonine, first noticed by Laurent, was proved by Greville Williams to exist, not only in these, but also in that prepared from coal-tar; hence all statements with the exception of those of Gr. Williams refer to impure chinoline.

*Formation.* 1. In the dry distillation of coal, in which case it mixes with the coal-tar. (Runge.) — 2. In the distillation of quinine, cinchonine, and strychnine with hydrate of potash. (Gerhardt.) — 3. By the electrolysis of nitrate of cinchonine. (v. Babo.) The liquid which has been exposed to the zinc-pole is deep reddish brown, and contains much separated resin. When this is removed and potash added, the liquid yields by gentle heating a caking precipitate, and evolves an odour of ammonia, and then at a stronger heat an odour of chinoline; the liquid decanted from the precipitate and distilled, yields an alkaline, milky distillate, together with drops of oil, which, both by their odour and by their reaction with sulphate of ethyl (p. 247) are proved to be chinoline. (von Babo.) — 4. On distilling thialdine with hydrate of lime, being recognisable by its odour and by the formation of the platinum-salt. (Wöhler, and Liebig, *Ann. Pharm.* 61, 5.) — 5. In the dry distillation of trigenic acid or trigenate of silver, chinoline passes over, having a sharp taste and strong alkaline reaction; after redistillation with caustic potash, it floats on the distillate in colourless oil-drops, which dissolve in hydrochloric acid, and form a crystalline double salt with bichloride of platinum. (Liebig and Wöhler, *Ann. Pharm.* 59, 289.) — 6. Chromate of pelosine decomposes at a temperature somewhat above  $100^{\circ}$ , giving off chinoline and carbolic acid, and leaving chromic oxide mixed with charcoal. (Bödeker, *Ann. Pharm.* 69, 59.) — 7. Berberin distilled with milk of lime or hydrated oxide of lead, yields chinoline, recognisable by its odour and by the deportment of the distillate slightly acidulated with hydrochloric acid, towards chloride of mercury. (Bödeker, *Ann. Pharm.* 69, 43.)

*Preparation.* 1. *From Quinine or Cinchonine.* — *a.* When 1 part of quinine is heated to ebullition with 4 parts of hydrate of potash and 1 part of water, the quinine turns brown, evolves hydrogen, swells up, and yields a distillate of water containing ammonia and feebly coloured chinoline, which is freed from the admixed ammonia by exposure to the air for 24 hours. (Gerhardt.) — *b.* When one part of cinchonine is distilled with 3 parts hydrate of potash and one-fourth part water, a considerable quantity of water passes over at first, then the residue froths up, gives off hydrogen abundantly, assumes a purple-red colour, and yields a distillate of chinoline mixed with water. A few drops of water are frequently added (since the retort would otherwise be attacked, and ammonia and a brown burnt mass be formed) and the distillate containing a little ammonia is rectified. This distillate becomes turbid when heated, gives off water and all the ammonia, then becomes clear, and yields first aqueous and afterwards anhydrous chinoline. (Bromeis.) Or powdered cinchonine is gradually added to hydrate of potash, which is heated in a retort till it melts, and then to a higher temperature till the cinchonine becomes brown and emits stifling vapours. (Gerhardt.)

According to Gr. Williams, all the chinoline obtained by the first



method is a mixture of several bases; he therefore subjects the crude chinoline obtained by the gradual distillation of cinchonine with hydrate of potash to ebullition with acids for several days, by which process pyrrhol is driven off. The dry chinoline afterwards separated begins to boil at  $149^{\circ}$ , but does not pass over in considerable quantity till the boiling point rises to  $183^{\circ}$ . Williams therefore separates it, by (200 times) repeated fractional distillations, into several portions, the lowest of which boils between  $154^{\circ}$ — $160^{\circ}$ , and the highest, which is the largest quantity, at  $271^{\circ}$ . Of these fractions, that which distils below  $165^{\circ}$  contains lutidine, with a little pyridine and picoline; that between  $177^{\circ}$  and  $182^{\circ}$  contains collidine, which is also found in the products up to  $199^{\circ}$ ; and that portion which distils above  $199^{\circ}$ , especially that between  $216^{\circ}$  and  $243^{\circ}$ , consists of chinoline and lepidine, the latter of which substances is chiefly found in the part boiling above  $270^{\circ}$ . For the preparation of chinoline (and of the other bases) in a perfectly pure form, he converts the individual fractions into platinum double salts, and effects the separation of the bases by fractional crystallisation.

2. *From Coal-tar-oil.* — (Comparexi, 217, b.) — *a.* The oily mixture of aniline and chinoline (leucol) obtained according to xi, 247, 3, is distilled until a drop passing over no longer forms a blue colour with hypochlorite of lime; all the aniline has then passed over, together with some portion of the chinoline, and chinoline alone remains behind. This residue is distilled with a fresh receiver, dehydrated by leaving it for some days in contact with hydrate of potash, and twice rectified in a stream of hydrogen. (Hofmann.) — *b.* The mixture of aniline and chinoline, obtained according to xi, 248,  $\beta$ , is converted into the oxalate; the mother-liquor, decanted from the oxalate of aniline which has crystallised out, is distilled with potash, the receiver being changed when the distillate no longer blues hypochlorite of lime; and the chinoline which then distils over is collected apart. (Hofmann.)

Since coal-tar-oil contains, besides chinoline, the homologous bases lepidine and cryptidine, as well as many others, Greville Williams treats 50 gallons of oil of a very high boiling point and higher specific gravity than water, with sulphuric acid; distils the acid liquid with lime; and takes from the distillate the portion which sinks to the bottom in water for further manipulation. He decomposes the admixed bases of the aniline series with nitrite of potash and hydrochloric acid; pours off the acid liquid from the heavy oil containing hydrate of phenyl; expels non-basic admixtures by passing steam through the liquid; filters the residue through charcoal; and separates the bases by means of hydrate of potash. These bases, when separated from the aqueous solution and dried over sticks of caustic potash, give, after more than 100 fractional distillations, portions boiling between  $177^{\circ}$  and  $274^{\circ}$ ; and from these the chinoline is separated in the manner above described (1).

*Properties.* Transparent, colourless, mobile oil (Runge), which neither thickens nor freezes at  $20^{\circ}$ . (Hofmann, Bromeis.) Sp. gr. 1.081 at  $10^{\circ}$  (Hofmann), 1.084 at  $16^{\circ}$ . (Bromeis.) Refracts light very strongly, like bisulphide of carbon. Index of refraction = 1.645. (Hofmann.) Conducts the electric current even less readily than aniline. (Hofmann.) Boils steadily at about  $238^{\circ}$  (Gr. Williams), with slight decomposition at  $239^{\circ}$  (Hofmann), and evaporates even at ordinary tempera-



tures; hence the oil-stain produced by chinoline on paper soon disappears. (Bromeis.) The vapour-density of chinoline boiling between  $238^{\circ}$ — $243^{\circ}$  is 4.519. (Gr. Williams.) Chinoline has a penetrating odour, recalling that of phosphorus and that of hydrocyanic acid (Runge); like St. Ignatius' beans (Gerhardt), like bitter almond-oil (Hofmann), ultimately suggestive of hydrocyanic acid. (Bromeis.) Its taste is sharp and very bitter (Gerhardt); more burning than that of aniline. (Hofmann.) It does not appear to be poisonous. (Gerhardt.) The aqueous solution kills leeches. 0.5 gr. with water in the stomach of a rabbit produces convulsive jerking back of the head, prostration of strength lasting several hours, no enlargement of the pupil, after which the animal recovers. When introduced into the eye, it produces contraction of the pupil. (Hofmann.) Chinoline produces an alkaline reaction in litmus and turmeric (Gerhardt, Bromeis); only on dahlia paper. (Hofmann.) Does not colour either aqueous hypochlorite of lime or pine-wood. (Runge.)

				Hoffmann. mean. <i>From coal-tar.</i>	Bromeis. mean. <i>From cinchonine.</i>
18 C	.....	108	...	83.72	..... 82.36
N	.....	14	...	10.85	..... 11.27
7 H	.....	7	...	5.43	..... 6.30
<hr/>					
C <sup>18</sup> NH <sup>7</sup>	.....	129	...	100.00	..... 99.93

	Vol.		Density.
C-vapour .....	18	.....	7·4880
N-gas .....	1	.....	0·9706
H-gas .....	7	.....	0·4851
<hr/>			
Chinoline-vapour .....	2	.....	8·9437
	1	.....	4·4718

The older formulæ were  $C^{18}NH^8$ , proposed by Hofmann;  $C^{16}NH^{11}O$ , by Gerhardt;  $C^{18}NH^8$ , by Bromeis; and lastly,  $C^{18}NH^7$  by Laurent, and  $C^{20}NH^9$  by Gerhardt. (*Traité*, 4, 149.) According to Gr. Williams, the chinoline of Hofmann and Bromeis contained lepidine.

*Decompositions.* 1. Chinoline, when set on fire, burns with a luminous smoky flame. (Hofmann.)—2. It becomes resinised in the air. (Hofmann.)—3. It undergoes considerable alteration when distilled alone (Gerhardt); leaves a slight yellow residue. (Hofmann.) The change observed by Gerhardt depends, according to Bromeis, on a separation of water. Gr. Williams was also able to determine the vapour density, in which Hofmann failed, probably on account of impurity of his chinoline. (See above.)

4. *Chlorine* instantly changes chinoline into a black resin, with violent disengagement of heat and evolution of hydrochloric acid. (Hofmann.) Chinoline dropped into a vessel containing chlorine, forms a yellow oil, which is decomposed by water, leaving a white insoluble substance. (Gr. Williams.)

5. *Bromine* forms with chinoline and aqueous salts of chinoline, a resin similar to that produced by chlorine, this resin, which is insoluble in water but dissolves in alcohol and ether, separating out as an amorphous mass. (Hofmann.)

6. On treating aqueous chinoline with a mixture of *hydrochloric acid* and *chlorate of potash*, the liquid is rapidly covered with a layer of orange-red oil, which solidifies on cooling to a tough mass which is insoluble in water, but easily soluble in warm alcohol, and on cooling from this solution, forms an amorphous precipitate which does not yield picric acid when treated with nitric acid. (Hofmann.)

7. By *fuming nitric acid* chinoline is but slowly attacked (so that even after five times pouring back the acid which has distilled off, potash still separates most of the chinoline unaltered) but is ultimately converted, if the acid is in great excess, into a brown, bitter, resinous mass, which can be drawn out into threads, becomes brittle on cooling, dissolves easily in potash, but is not picric acid. (Hofmann.) Fuming nitric acid acts violently on chinoline, and converts it into a splendid mass of crystals, but does not form any products of decomposition. (Gr. Williams.)

8. Chinoline immediately takes fire in contact with dry *chromic acid*. It is resinized by aqueous chromic acid. (Hofmann, see page 249.)

9. *Permanganate of Potash* decomposes chinoline into oxalic acid and ammonia. (Hofmann.)

10. *Potassium* dissolves in chinoline with evolution of hydrogen, but without colouring. On melting potassium in chinoline vapour, cyanide of potassium is formed. Chinoline vapour passed over burnt tartar remains for the most part unchanged, but forms a small quantity of cyanide of potassium. (Hofmann.)

11. Chinoline passed over *red-hot quick lime* (Hofmann), or *soda-lime* (Bromeis), suffers little or no decomposition.

12. Enclosed in a sealed tube with *iodide of methyl*, and heated for ten minutes to 100°, chinoline is changed into crystals of hydriodate of methyl chinoline. In like manner, it is converted by *iodide of ethyl* into hydriodate of ethyl-chinoline, and by *iodide of amyl* into hydriodate of amyl-chinoline. (Williams.)

13. Chinoline becomes warm when mixed with *sulphate of methyl* (sometimes disengaging vapour of methylic ether and methylic alcohol), and forms, if complete combination has been promoted by heat, a liquid soluble in water, which, when excess of sulphate of methyl is present, deposits separate crystals. The liquid is rendered turbid by potash or baryta, and separates oil-drops, which at first become red, then green, finally violet, and when heated pass into a beautiful violet resin, *Methylirisine*, with formation of sharp, strongly smelling, condensable vapours. At the same time, a brown resin and a sulphomethylate are formed. Chinoline heated to boiling with *sulphate of ethyl*, forms a colourless liquid, which on boiling with strong caustic potash, deposits a violet resin, *ethylirisine*, insoluble in ether, and a brown resin soluble in ether, while a sulphovinate remains dissolved, and a sharp, neutral oil, sinking in water, passes over, which, if immediately mixed with bichloride of platinum yields beautiful needles, but soon decomposes. (v. Babo.)

14. *Chloride of acetyl* acts violently on chinoline, forming a crystalline very deliquescent mass. (Williams.)

15. With *Anilocyanic acid*, chinoline solidifies into a crystalline mass of carbanilide-carbohinoline. (Hofmann.)

*Combinations. With Water.* — *a. Monohydrated Chinoline.* — When chinoline saturated at 0° with water is heated to 100°, water and a little chinoline escape, and the chinoline becomes quite clear. (Bromeis.)

					Bromeis. mean.
16 C .....	108	...	78.26	.....	78.02
N .....	14	...	10.14		
8 H .....	8	...	5.80	.....	6.48
O .....	8	...	5.80		
<hr/> C <sup>18</sup> NH <sup>7</sup> + Aq.....					138 .... 100.00

This hydrate remains limpid and mobile at 20°. (Bromeis.) It is decomposed by distillation into water and anhydrous chinoline.

*b. Terhydrated Chinoline.* — Chinoline shaken up with cold water at 0° forms a clear oil saturated with water, which becomes turbid at 15°, with separation of water. (Bromeis.)

					Bromeis. mean.
18 C .....	108	...	69.23	.....	69.77
N .....	14	...	8.97		
10 H .....	10	...	6.42	.....	7.08
4 O .....	24	...	15.38		
<hr/> C <sup>18</sup> NH <sup>7</sup> + 3Aq.....					156 .... 100.00

Compare also Laurent (*N. Ann. Chim. Phys.* 19, 367), and Gerhardt (*Traité*, 4, 149), who doubt the existence of definite hydrates.

*Aqueous Chinoline.* — Chinoline is but sparingly soluble in water (Gerhardt); more soluble in hot than in cold water. (Hofmann.) The alkaline solution becomes milky when more chinoline is added to it. (Gerhardt.) Ether extracts it from the water. (Hofmann.)

Chinoline dissolves *phosphorus, sulphur, and arsenic* like aniline. It mixes in all proportions with bisulphide of carbon. (Hofmann.)

Chinoline unites with acids, the mixture becoming heated, and forms the chinoline-salts. (Hofmann.) It precipitates the salts of alumina, and renders lead-salts and ferrous sulphate slightly turbid. It precipitates ferric salts (Hofmann); aqueous chinoline precipitates nitrate of silver, but not ferric nitrate. (Gerhardt.) — The salts of chinoline crystallise readily (Gerhardt, Williams); with difficulty. (Hofmann.) When prepared by saturating chinoline with acid, they smell of vegetable juice, but not after recrystallisation. (Gerhardt.) The fixed alkalies separate chinoline from them, which forms a clear oily layer after some time only; similarly ammonia decomposes them at a moderate heat, but at a high temperature ammonia is expelled by chinoline. (Hofmann.) From dry chinoline-salts aniline evolves the odour of chinoline. (Hofmann.)

*Sulphate of Chinoline.* — Beautiful, white, radiating crystals, easily soluble in water and alcohol. (Gerhardt.) — Anhydrous, aqueous, or alcoholic chinoline, mixed with sulphuric acid, leaves a viscid syrup when evaporated over oil of vitriol. From an ethereal solution of chinoline, strong sulphuric acid precipitates a gummy liquid, which sinks down, and after standing under the ether for a few days solidifies into a deliquescent crystalline mass. (Hofmann.)

*Hydrochlorate of Chinoline.* — Chinoline forms slight fumes with hydrochloric acid. (Hofmann.) Slender needles. (Gerhardt.) Chinoline, whether

anhydrous or in aqueous solution, violently absorbs dry hydrochloric acid gas, with disengagement of heat. On cooling, the mass soon solidifies to white crystals, which take up more hydrochloric acid, become red and liquid, and on again cooling, solidify to a radiant, deliquescent and strongly acid crystalline mass. Hydrochloric acid appears therefore to form with chinoline both an acid and a neutral salt. (Bromeis.) Chinoline saturated with hydrochloric acid dries to a thick syrup in the vacuum of the air-pump. When dry hydrochloric acid is passed over chinoline dissolved in ether, hydrochlorate of chinoline precipitates in heavy viscous drops, which after a while become slightly crystalline. (Hofmann.)

*Nitrate of Chinoline.* — Slender needles. (Gerhardt.) The amber-yellow solution of chinoline in dilute nitric acid yields, on evaporation over oil of vitriol, concentrically grouped needles which may be obtained white and dry by pressing between paper, and are readily crystallised from alcohol. Exposed to the air, they become blood-red. When carefully heated, they melt to a clear oil, and if further heated, they form a colourless gas, which on cooling covers the sides of the tube with a crystalline deposit. (Hofmann.) The solution of chinoline in excess of nitric acid leaves, on evaporation in the water-bath, a pasty mass which solidifies on cooling, and from the hot alcoholic solution of which, white needles are obtained, permanent in the air, not fusible at  $100^{\circ}$ , and consisting of  $C^{18}NH^7,HO,NO^5$ . (Williams.) The salt dissolves easily in water and alcohol, but is insoluble in ether. (Hofmann.)

*Chromate of Chinoline.* — Chromic acid forms with chinoline a yellow crystalline precipitate. (Gerhardt, Hofmann.) — *Bichromate.* — Excess of dilute chromic acid precipitates from chinoline a small quantity of a resinous matter which becomes crystalline when rubbed with a glass rod, dissolves in boiling water after filtering and washing, and is deposited in brilliant needles on cooling. Detonates when heated, but not after addition of hydrochloric acid. (Williams.) Williams could not obtain a crystallised compound with the chinoline from gas-tar, even when the impurities which could be destroyed by chromic acid were removed, but only oily drops.

<i>At 100.</i>				Williams.	
18 C	.....	108	....	45.11	..... 45.08
N	.....	14	....	5.84	
8 H	.....	8	....	3.34	..... 3.49
2 Cr	.....	53.4	....	22.31	..... 22.34
7 O	.....	56	....	23.40	
<hr/>					
$C^{18}NH^7,HO,2CrO^3$				..... 239.4	.... 100.00

*Chloride of Uranyl with Hydrochlorate of Chinoline.* — On mixing concentrated solutions of ammonio-chloride of uranyl and hydrochlorate of chinoline, the liquid solidifies; from dilute solutions beautiful yellow prisms are obtained. (Tr. Williams.)

At 100°.				Williams.
18 C .....	108	...	32.05	..... 31.87
N .....	14	...	4.15	
8 H .....	8	...	2.37	..... 2.77
2 Cl .....	71	...	21.07	..... 20.97
2 U .....	120	...	85.61	
2 O .....	16	...	4.75	
<hr/>				
$C^{18}NH^7, HCl, U^2O^2Cl$ .....	337	...	100.00	

Chinoline produces with *terchloride of antimony* a white precipitate which, when dissolved in boiling hydrochloric acid, is obtained in crystals on cooling. (Hofmann.)

*Chloride of Cadmium with Hydrochlorate of Chinoline.* — The concentrated solutions of the two salts solidify to a pulp when brought together; the dilute solutions yield white, permanent needles an inch long, which at 100° give off 2 At. water, and then consist of  $C^{18}NH^7, HCl, 2CdCl$ , and volatilise completely at a higher temperature. Sparingly soluble in alcohol. (Williams.)

With *protochloride of tin*, hydrochlorate of chinoline produces a yellow heavy oil which afterwards becomes crystalline, and dissolves with difficulty in alcohol. (Hofmann.)

Chinoline precipitates from *sulphate of copper*, a light blue compound unchanged by boiling. (Hofmann.) Aqueous chinoline does not precipitate sulphate of copper. (Gerhardt.)

*Chloride of Mercury with Chinoline.* — Chloride of mercury produces in hydrochlorate of chinoline, a white, non-crystalline precipitate, and the liquid separated therefrom, deposits on evaporation, spangles having a satiny lustre. (Gerhardt.) The white precipitate dissolves readily when warmed, and separates on cooling in beautiful pearly plates, which at a little above the mean temperature, are at first red, and then become black. (Bromeis.) Tastes very bitter, and unpleasantly metallic; smells of chinoline. — The solution of chinoline in a large quantity of alcohol is precipitated by chloride of mercury. (With too little alcohol, a greasy mass would be formed.) White crystalline precipitate which is not decomposed by boiling with water. (Hofmann.)

				Hofmann.
18 C .....	108	...	27.00	..... 26.49
N .....	14	...	3.50	
7 H .....	7	...	1.75	
2 Cl .....	71	...	17.75	..... 17.57
2 Hg .....	200	...	50.00	..... 49.90
<hr/>				
$C^{18}NH^7, 2HgCl$ .....	400	...	100.00	

*Gold salt of Chinoline.* — Chinoline and hydrochlorate of chinoline form a white precipitate with *terchloride of gold*. (Gerhardt.) — Delicate, canary-yellow needles, which are quite permanent in the air, and after drying at 100° contain 41.85 per cent. of gold, and are therefore  $C^{18}H^7N, HCl + AuCl^3$ . (Calculation = 42.0 p. c. gold). Sparingly soluble in water. (Williams.)

**Platinum-salt.** — When crude chinoline is dissolved in a slight excess of hydrochloric acid, and chloride of platinum added, a yellow precipitate is at once formed (crystalline, according to Hofmann and Bromeis); this precipitate is collected on a filter and recrystallised from boiling water, which deposits it on cooling in golden yellow needles. (Gerhardt, Bromeis.) Chloroplatinate of ammonium, and other impurities remain on the filter (Gerhardt); they are deposited first from the solutions. (Bromeis.) Hofmann washes the salt with alcoholic ether, because water and hydrochloric acid dissolve it slightly. — When pure, it is immediately deposited in the crystalline form from the hot saturated solution, so that the supernatant liquor remains clear. (Gerhardt.)

Golden-yellow needles (Gerhardt); beautiful, tufted needles. (Bromeis.) Orange-yellow, somewhat lighter than chloroplatinate of aniline. Scarcely loses weight at 100°. (Hofmann.) Dissolves in 893 parts of water at 15.5° (Williams); the aqueous solution as well as the solution in dilute hydrochloric acid, form nodular deposits by slow evaporation. (Gerhardt, Bromeis.) Sparingly soluble in alcohol and ether. (Hofmann.)

				Gerhardt.	Bromels.
				<i>from Quinine.</i>	<i>from Cinchonine.</i>
				<i>mean.</i>	<i>mean.</i>
<i>At 100°.</i>					
18 C .....	108	....	32.22	..... 32.65	..... 33.36
N .....	14	....	4.18	..... 4.42	..... 4.06
8 H .....	8	....	2.39	..... 3.19	..... 2.74
Pt ....	98.7	....	29.44	..... 27.94	..... 28.33
3 Cl .....	106.5	....	31.77		
<hr/>					
$C^{18}NH^7, HCl + PtCl^2$ ....	335.2	....	100.00		

				Hofmann.	Williams.
				<i>from Coal-tar.</i>	<i>from Cinchonine.</i>
					<i>mean.</i>
<i>At 100°.</i>					
18 C .....	108	....	32.22	..... 32.06	..... 32.86
N .....	14	....	4.18		
8 H .....	8	....	2.39	..... 2.58	..... 2.74
Pt .....	98.7	....	29.44	..... 29.19	..... 29.29
3 Cl .....	106.5	....	31.77	..... 30.96	
<hr/>					
$C^{18}NH^7, HCl + PtCl^2$ ....	335.2	....	100.00		

When prepared from cinchonine, it contains 27.69; from strychnine 27.58 p. c. platinum. (Gerhardt.) According to Williams, it always contains chloroplatinate of lepidine, unless this base has been removed by fractional crystallisation. Laurent also observed that the platinum-salt of chinoline contained two kinds of crystals.

**Palladium-salt.** — Chinoline precipitates chloride of palladium like aniline. (Hofmann.) Chestnut-brown crystals which contain 20.96 p. c. Pd and are therefore  $C^{18}NH^7, HCl, PdCl$ . (Calculation = 21.18 p. c.) Sparingly soluble in water. (Williams.)

**Oxalate of Chinoline.** — Slender needles, which emit a phosphoric odour in contact with the moist skin. Crystallises readily. (Runge.) Confused, radiating, unctuous mass, which dissolves easily in water, alcohol and ether. (Hofmann.) — **Binoxalate.** — Obtained by dissolving 24.3 parts of chinoline, and 16.5 parts of dry oxalic acid in small quan-

tities of water and evaporating the mixed solutions. White, soft, crystalline mass, converted by repeated recrystallisation from alcohol, into lustrous, silky needles, consisting of  $C^{18}H^7N, C^4H^2O^8$ ; decomposed at  $100^\circ$  with evolution of chinoline. (Williams.)

When chinoline containing aniline is dissolved in alcohol or ether, and mixed with alcoholic oxalic acid, almost all the oxalate of aniline is deposited after a few hours, while the oxalate of chinoline remains in solution. (Hofmann.)

*Picrate of Chinoline* resembles picrate of aniline in every respect.

*Formiate of Chinoline.* — Chinoline gives a yellowish brown precipitate with infusion of galls. (Hofmann.) White flocculent precipitate which dissolves in boiling water and in alcohol. (Gerhardt.)

Chinoline mixes in all proportions with *alcohol* and *ether* (Gerhardt), also with *wood-spirit*, *aldehyde* and *acetone*. (Hofmann.) Ether takes it up from the aqueous solution. (Hofmann.)

It mixes with volatile (Gerhardt) and fatty oils (Hofmann); dissolves common camphor, and resin like aniline, but not copal or caoutchouc. It does not coagulate albumen. (Hofmann.)

### *Conjugated compounds containing the nucleus $C^{18}NH^5$ .*

#### **Methylchinoline.**



GR. WILLIAMS. *J. pr. Chem.* 69, 360.

*Formechinolin, Methylchinolin.*

Known only in combination with acids.

*Preparation of Hydriodate of Methylchinoline.* — When chinoline is heated with iodide of methyl in a sealed tube to  $100^\circ$  for ten minutes, beautiful crystals of hydriodate of methylchinoline are obtained.

This salt is decomposed by oxide of silver, forming iodide of silver, and an unstable, strongly alkaline solution, which, when heated with potash, produces a suffocating odour, probably arising from methylamine.

*Platinum-salt.* — The solution of crystallised hydriodate of methylchinoline is decomposed, first by nitrate of silver, and then by hydrochloric acid; on then adding bichloride of platinum, a sparingly soluble platinum-salt is obtained. (Williams.)

						Williams.
20 C	.....	120	....	34.33	.....	34.59
N	.....	14	....	4.01		
10 H	.....	10	....	2.86	.....	3.06
Pt	.....	99	....	28.33	.....	28.20
3 Cl	.....	106.5	....	30.47		
<hr/>						
$C^{20}H^9N, HCl + PtCl^2$	....	349.5	....	100.00		



*Appendix to Methylchinoline.***Methylirisine.**

VON BABO. *J. pr. Chem.* 72, 18.

*Formation* (p. 247, 13).

*Preparation.* Chinoline is heated with sulphate of methyl until combination has taken place, and potash or baryta is added to the liquid: the violet resin thereby formed is separated by filtration from the alkaline solution, and dissolved in water; sulphuric acid is added till the violet colour disappears, and the whole is evaporated nearly to dryness. The residue treated with baryta-water till the sulphuric acid is precipitated, again forms a violet solution, which is mixed with 4 times its bulk of absolute alcohol, freed from baryta by carbonic acid, then filtered, and evaporated to dryness; on subsequently washing out the residue with ether, methylirisine remains undissolved.

*Properties.* Violet, tough, amorphous mass, having a splendid coppery lustre; on exposure to the air, it acquires a beautiful green colour and the lustre of cantharides, and when heated, becomes again violet-brown, with loss of water. In the dry state, it can be heated to 150° without change. Not volatile without decomposition.

*Decompositions.* 1. Burns on platinum, giving off vapours like aniline. — 2. Rapidly decomposed by excess of acids, by oxidising agents, chlorine, nitric acid, and sesquichloride of iron. — 3. Decomposed by boiling in acid solution with bichloride of platinum.

Dissolves in water with a bluish dark red colour, and concentrated potash-ley precipitates methylirisine from the solution as a flocculent resin. The concentrated aqueous solution transmits the orange and yellow rays of the spectrum, part of the blue near the violet, and part of the violet rays; after dilution, the orange-coloured rays near the red, and the yellow rays near the green increase, those near the green more slowly; the blue rays lying near the violet increase only after great dilution.

Methylirisine dissolves in acids. The concentrated solution is brown, the dilute solution colourless. The solutions leave on evaporation an amorphous residue, which, when strong acids have been used, retains a portion of the acid.

By potash, carbonate of baryta, or carbonate of lime, they are immediately coloured blue, with loss of acid; by the former, a resinous precipitate is produced. They are completely precipitated by the chlorides of mercury and of platinum; the violet-grey precipitates are coloured violet by potash and decomposed. The solution in acetic acid gives off acid on evaporation, and becomes violet. The dilute aqueous solution is completely decolorised by a very small quantity of free acid, and may hence be used instead of litmus for the detection of free acid, or of free alkali, which restores the colour.

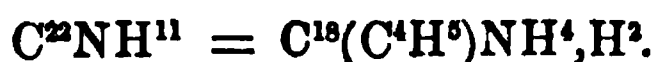
Methylirisine dissolves readily in alcohol, the colour of the solution varying from a violet to an indigo-blue. The solution completely trans-



mits the orange, blue and indigo rays of the spectrum; after dilution with alcohol, the orange increases towards the red, but not towards the yellow; the blue also increases towards the green, and only after considerable dilution, towards the violet. After diluting the alcoholic solution with water, the orange increases towards the yellow and green; blue, more slowly towards the green, and only when greatly diluted towards the violet.

Methylirisine is insoluble in ether.

### Ethylchinoline.



GR. WILLIAMS. *J. pr. Chem.* 69, 360.

*Vinechinolin.* — Supposing it to contain an additional atom of hydrogen, it would become *ethylchinolinammonium*. Known only in combination with acids.

Chinoline treated with iodide of ethyl, as in the preparation of hydriodate of methylchinoline, yields, after distilling off the excess of iodide of ethyl, crystals of hydriodate of ethylchinoline. These crystals are treated with oxide of silver and water (if this is done in the water-bath, a volatile product escapes which attacks the eyes) and after filtering off the iodide of silver, a colourless, strongly alkaline solution of ethylchinoline is obtained.

The solution decomposes on evaporation in the water-bath, assuming a carmine colour, emerald-green on the edges, afterwards changing to a beautiful blue. It expels ammonia from sal-ammoniac. It precipitates chloride of mercury and the salts of lead, iron and copper.

*Hydriodate of Ethylchinoline* forms cubes when recrystallised from alcohol. It is more soluble in water than in alcohol.

At 100°.				Williams.	
22 C .....	132	....	46.32	.....	46.53
N .....	14	....	4.91		
12 H .....	12	....	4.21	.....	4.41
I .....	127	....	44.56	.....	44.12
<hr/>					
$C^{22}H^{11}N, H^7$ ....	285	....	100.00		

At 100° it becomes transiently blood-red. It is decomposed by sulphate of silver, forming iodide of silver, and a liquid which is colourless at first, but on evaporation over the water-bath, assumes a carmine colour, dark blue at the edges, and when dry leaves a blackish-red mass having a coppery lustre. The mass forms with water a dark carmine solution, which is coloured scarlet by hydrochloric and nitric acids, and rose-red by ammonia: with potash, it forms a violet precipitate which is little soluble in water, but dissolves in alcohol, forming a carmine-red solution. Bichloride of platinum produces in the hydrochloric acid solution of the precipitate, a bulky, insoluble double salt of a higher atomic weight than the platinum-salt of hydrochlorate of ethylchinoline.

*Platinum-salt of Ethylchinoline.* — Golden yellow, sparingly soluble precipitate, consisting of  $C^{22}H^{11}, HCl, PtCl^2$ . (Williams.)

*Appendix to Ethylchinoline.***Ethylirisine.**

V. BABO. *J. pr. Chem.* 72, 85.

*Formation.* (p. 247, 13.)

*Preparation.* 1 part of chinoline is mixed with 2 parts of sulphate of ethyl; the mixture is heated to boiling till the combination is complete; and the solution, mixed with excess of concentrated potash ley, is boiled, with continual agitation, till the separated ethylirisine assumes a violet or almost indigo colour. The potash is then poured off; the residual resin again heated with water and potash-ley; the cherry-red liquid is decanted when cold; and this treatment is repeated until potash no longer takes up any sulphovinate (or methionate or ethionate), that is, when a small quantity of the product gives, after evaporation and ignition, little or no reaction for sulphuric acid. The remaining resin is dissolved in anhydrous alcohol and precipitated by the addition of a large quantity of ether; the ether poured off and replaced as long as a fresh portion becomes coloured; and lastly, the mass, exhausted with ether, is dissolved in alcohol and evaporated to dryness. If the residue still becomes moist in the air—in consequence of retaining potash,—it must be stirred with a little water and alcohol, by which the impurer part is extracted and pure ethylirisine left.

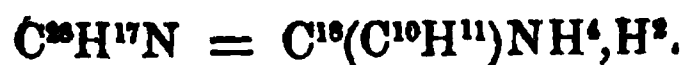
*Properties.* Blue pulverisable resin, having a coppery lustre, stronger than that of sublimed indigo.

Ethylirisine appears to be quickly decomposed by ammonia.

It is less soluble in water than methylirisine.

Dissolves in acids with reddish brown colour, which disappears on dilution, and is again brought out by alkalis. The solution in hydrochloric acid leaves a varnish-like coating when evaporated in vacuo. With chloride of platinum it forms a quickly decomposable double salt, of variable composition.

It dissolves in alcohol, forming a solution whose colour varies from deep violet to indigo, and becomes cherry-red on addition of water.

**Amylchinoline.**

GR. WILLIAMS. *J. pr. Chem.* 69, 361.

*Mylechinolin.*

Known only in combination with acids.

A mixture of iodide of amyl and chinoline heated in a sealed tube for several hours to 100°, deposits beautiful crystals of hydriodate of amylchinoline, which are  $C^{25}NH^{15}I$ . These crystals, treated with nitrate of

silver and then with hydrochloric acid, yield the hydrochlorate, from whose solution chloride of platinum precipitates chloroplatinate of amyl-chinoline, which is but sparingly soluble in water, and does not dissolve in ether-alcohol. After drying at  $100^\circ$ , it contains  $C^{20}NH^{18}Cl$ ,  $PtCl^2$ . (Williams.)

*Primary Nucleus  $C^{16}H^8$ .*

**Styrone.**



ED. SIMON. (1839.) *Ann. Pharm.* 31, 274; *N. Br. Arch.* 29, 182.

TOEL. *Ann. Pharm.* 70, 3.

STRECKER. *Ann. Pharm.* 70, 10; *Compt. rend.* 39, 61; *Ann. Pharm.* 93, 370; *J. pr. Chem.* 62, 448; *Pharm. Centr.* 1854, 672.

J. WOLFF. *Ann. Pharm.* 75, 299.

E. KOPP. *Compt. Chim.* 1850, 143.

SCHARLING. *Ann. Pharm.* 95, 90 and 183.

*Styraxalcohol, Styracol, Zimmtalcohol.* Obtained in an impure state by distilling storax freed from styrol and cinnamic acid = styracon.

Discovered and recognized as an alcohol, by Simon; more completely investigated by Toel; Strecker then observed the relations of styrone to cinnamic acid, and fixed the formula. Declared by E. Kopp to be identical with peruvine; a statement disproved by Scharling.

*Formation.* By the decomposition of styracin with potash (Simon, Toel); in small quantity by boiling oil of cinnamon with alcoholic potash (Limpricht, *Lehrbuch*, 539).

*Preparation.* 1. When styracin dissolved in alcohol is mixed with a great excess of soda, the liquid filtered from the cinnamate of soda thereby produced, and the filtrate evaporated, crystals of styrone separate out. (Simon.) Wolff dissolves styracin in boiling alcoholic potash, mixes water with the liquid, filters off from the cinnamate of potash, and separates the precipitated styrone from undecomposed styracin by distillation.

2. Styracin distilled with excess of concentrated potash, begins to froth up as the heat is increased, while cinnamate of potash remains in the retort, and is kept in solution, by addition of water. From the milky distillate, most of the styrone separates on cooling; the rest is obtained by saturating with salt and agitation with ether. (Toel.) Wolff uses potash-ley of sp. gr. 1.2 (weaker leys give off at first nothing but water; stronger ley decomposes the styrone itself); frees the residue from cinnamate of potash by adding hot water from time to time; distils the undissolved portion with fresh potash, which he keeps at the right strength by addition of water; shakes the whole distillate with ether, after saturation with salt; leaves the ether to evaporate in a warm place; and distils the residue over chloride of calcium. The distillate solidifies after a while into a hard crystalline mass.

By distilling storax freed from styrol and from cinnamic acid with aqueous soda-ley, Simon obtained a milky distillate, from which common salt separated styracone as a heavy oil, which when purified by filtration and rectification, did not exhibit a constant boiling point. (Simon.)— It boils at  $230^\circ$ , contains on an average 79.6 p. c. C, and 8.5 p. c. H, but the analyses of products of different preparation do not agree with one another.

(Scharling.) On distilling with very concentrated potash or soda-ley the resin remaining in the preparation of styracin (p. 287, 6), after it had been freed by kneading from most of the styracin, E. Kopp obtained a milky distillate, which he purified in the same manner as Simon; it then boiled at  $254^{\circ}$ , crystallised in the cold, melted at  $8^{\circ}$ , and smelt of grape-stones. According to Scharling, this body comports itself in the air towards platinum black, and towards powdered hydrate of potash and bisulphide of carbon, like styrone. According to Simon, it is a product of the decomposition of styrone.

**Properties.** Colourless, long, thin, silky needles. (Toel.) Melts at  $19^{\circ}$  (Simon), at  $33^{\circ}$  (Toel), and solidifies in the crystalline form. It evaporates undecomposed at a higher temperature. (Toel.) Boils at  $250^{\circ}$ . (Wolff.) Has a very pleasant smell of hyacinths. (Toel.)

					Toel. mean.		Wolff. mean.
18 C	.....	108	...	80.62	.....	80.20	.... 80.45
10 H	.....	10	...	7.45	.....	7.64	.... 7.50
2 O	.....	16	...	11.93	.....	12.16	.... 12.05
<hr/>							
$C^{18}H^{10}O^2$	.....	134	...	100.00	.....	100.00	.... 100.00

Toel formerly proposed the formula  $C^{12}H^{23}O^5$ .

**Decompositions.** Exposed in an open tubulated retort to the air and to light, it slowly gains weight (chiefly, perhaps, by attracting water); remains solid at first; then melts (on the 11th day); and again solidifies; afterwards (from the 12th day), it remains fluid, and emits an odour of bitter almond oil and vapours which redden litmus, although bisulphite of potash does not shew that the former is present, nor can benzoic or cinnamic acids be extracted by carbonate of soda. The greater part of the styrone remains unchanged at the end of 16 months. (Scharling.)

2. Styrone exposed to the air, in contact with *platinum black*, changes in a few days into cinnamic aldehyde. (Strecker.)

3. Styrone does not dissolve in hot *nitric acid*, and is but very slowly attacked by it. When it is distilled with a large quantity of nitric acid, much nitrous acid is given off, hydride of benzoyl passes over, and the crystallised residue consists of benzoic acid, both being produced by the secondary action of the nitrous acid on the cinnamic acid at first formed. Hence if the distillation be made in the manner just described, but with addition of urea, much less hydride of benzoyl is obtained and the residue consists of nitrocinnamic acid. (Wolff.)

4. Yields hydride of benzoyl by distillation with *peroxide of manganese* and sulphuric acid. (Toel.)

5. Becomes strongly heated with *chromic acid*, or with chromate of potash and sulphuric acid, and on cooling, cinnamic acid separates, occasionally crystalline, but generally amorphous and coloured by chromic oxide. (Wolff.)

6. Styrone solidifies when heated with concentrated potash and *peroxide of lead*, and if the heat be continued, melts and forms oxide of lead, or even metallic lead, giving off a considerable quantity of hydride of benzoyl, and leaving cinnamate of potash.

7. Very concentrated *potash-ley* heated with styrone, colours it yellow, then red, and lastly, when the ley has almost become hydrate of potash, dark brown, without dissolving it. Most of the styrol distils

over unchanged; the residue dissolves in water, and forms with acids a white precipitate whose solution in alcohol or ether leaves a tough uncrySTALLISABLE oil when evaporated. (Wolff.)

8. When fuming *sulphuric acid* is poured over styrene, the latter becomes purple, solidifies to a crystalline mass, and forms a neutral soluble salt with baryta. (Wolff.)

9. Styrene dissolved in rock-oil and treated with powdered *hydrate of potash* and *bisulphide of carbon*, forms a salt resembling xanthate of potash, which gives a brown precipitate, afterwards turning yellow, with cupric salts, and a white precipitate with nitrate of lead. This salt may be recrystallised from a little water, but in the impure state it is decomposed by an excess of water. (Scharling.)

*Combinations.* Styrene is moderately soluble in *water*. The solution in hot water becomes milky on cooling, and when examined by the microscope exhibits numerous oil-drops, but becomes clear after a few minutes, in consequence of the crystallisation of the styrene. Dissolves very easily in *alcohol*, in *ether*, in *styrol*, and in *oils* both volatile and fatty. (Toel.)

### Cinnamic Aldehyde.



BLANCHET. *Ann. Pharm.* 7, 163.

DUMAS & PELIGOT. (1834.) *Ann. Chim. Phys.* 57, 305; *J. pr. Chem.* 3, 57; *Ann. Pharm.* 14, 50.

MULDER. *Pogg.* 41, 398; *J. pr. Chem.* 18, 385; *Ann. Pharm.* 34, 147.

MARCHAND. *J. pr. Chem.* 17, 303.

PERSOZ. *Compt. rend.* 13, 433; *J. pr. Chem.* 25, 99.

BERTAGNINI. *Ann. Pharm.* 85, 271.

AD. STRECKER. *Compt. rend.* 39, 61; *Pharm. Centr.* 154, 672; *Ann. Pharm.* 93, 370; *J. pr. Chem.* 62, 448.

CHIOZZA. *Ann. Pharm.* 97, 350.

PIRIA. *Ann. Pharm.* 100, 104.

A. GÖSSMANN. *Ann. Pharm.* 100, 57.

*Zimmtaldehyd, Zimmtöl, Cassiaöl, Hydrure de cinnamyl, Cinnamylwasserstoff.*

Dumas and Peligot observed in 1834, that oil of cinnamon consists for the most part of the aldehyde of cinnamic acid, and established its properties and composition.

*Sources.* Cinnamic aldehyde occurs, together with larger or smaller quantities of hydrocarbons, in the ethereal oils obtained by distilling with water the bark of *Cinnamomum aromaticum* and *Cinnamomum zeylanicum*. In the ethereal oil of cinnamon-blossom (Mulder); but not in the so-called oil of cinnamon-leaf from Ceylon. (Stenhouse.)

According to Mulder, oil of cinnamon is  $C^{20}H^{11}O^2$ , and the oil  $C^{18}H^8O^2$  is a product of decomposition.

*Formation.* 1. Cinnamic alcohol exposed to the air in contact with platinum black is converted into cinnamic aldehyde.



2. The aldehyde is formed by the distillation of cinnamate and formiate

of lime (Piria.) — 3. When a mixture of bitter almond oil and aldehyde is saturated with hydrochloric acid gas and heated, large quantities of hydrochloric acid gas and aldehyde are given off, after which the mixture becomes turbid, separates water, and yields, by distillation, first bitter almond oil, and then a little cinnamic aldehyde. (Chiozza.)

*Preparation.* Good Chinese cinnamon is bruised and softened with salt water, then quickly distilled, and the oil is dried over chloride of calcium. (Blanchet, Dumas & Peligot, Mulder.) The substance thus prepared consists of two oils, one lighter, and one heavier than water; they occur mixed in the commercial oil. The commercial oil from Ceylon cinnamon has a very pleasant odour and a golden yellow colour, paler after rectification; it boils at  $220^{\circ}$ , has a sp. gr. of 1.008 at  $25^{\circ}$ , and contains 81.44 p. c. C, 7.68 p. c. H, and 10.88 p. c. O. The commercial oil from cassia-cinnamon has a sharper odour, boils at  $225^{\circ}$ , and contains both oils, but probably in other proportions. Both the oils combine partially with baryta, to form a mass soluble in water, and with lime to form an almost insoluble mass, while the other portion easily resinifies. (Blanchet.) The oils from Ceylon cinnamon, Chinese cinnamon, cinnamon flowers, and Cortex Cassiæ, prepared by Mulder himself, the commercial oil of the Zoll company in Ceylon, and the Java oil of cinnamon were all found by Mulder to have the same composition, and contained 81.51 to 82.67 p. c. C, 6.90 to 7.48 p. c. H, and 9.98 to 11.32 p. c. O. Marchand found in the oil of cinnamon prepared by Mulder 81.8 p. c. C, 7.3 H, and 10.9 O. Göbel found in oil of cassia 76.7 p. c. C, 9.7 H, 13.6 O; in Ceylon oil of cinnamon 78.1 p. c. C, 10.9 H, and 11.0 O.

Oil of cinnamon is yellow (Margueron), after rectification paler (Blanchet), colourless. (Lewis.) Sp. gr. 1.035. (Lewis.) Freezes at a temperature several degrees below  $0^{\circ}$ , and then melts at  $5^{\circ}$ . (Margueron.) Has a sharp, burning, and sweetish taste; becomes turbid at  $20^{\circ}$  from deposition of camphor. (Bizio.)

The oil specially prepared, or the commercial oil, may be purified from the admixed hydrocarbons, from the cinnamic acid arising from the action of the air, and from the resinous products of decomposition, as follows:

1. It is shaken with concentrated nitric acid, whereupon pure oil of cinnamon immediately becomes a mass of crystals, and in the commercial oil there are formed, after two or three hours, large crystals of a compound of nitric acid with cinnamic aldehyde, which, when collected on a filter, so as to allow the still liquid portion to drain off, and then decomposed by water, yields pure cinnamic aldehyde. (Dumas and Peligot.)

2. The oil is shaken up with 3 or 4 times its volume of a solution of bisulphite of potash at  $28^{\circ}$  to  $30^{\circ}$  (Baumé); and the crystalline mass which forms in a few minutes with evolution of heat, is separated from the mother-liquor, allowed to dry on a filter, then pulverised and washed with cold alcohol, as long as the liquid runs off coloured and leaves a residue on evaporation, then again dried and dissolved at a gentle heat in dilute sulphuric acid. A large quantity of sulphurous acid is thereby disengaged, and the cinnamic aldehyde rises to the surface as a colourless oil, which has still to be freed from water and sulphurous acid. (Bertagnini.)

*Properties.* Colourless oil, heavier than water. Distils without decomposition, either in vacuo or with water which has been freed from air by boiling. (Mulder.)

				Dumas & Peligot.		Mulder.			
						<i>a.</i>		<i>b.</i>	
18 C .....	108	....	81.81	.....	80.64	....	80.12	....	80.65
8 H .....	8	....	6.06	.....	6.25	....	6.56	....	6.16
2 O .....	16	....	12.13	.....	13.11	....	13.32	....	13.19
<hr/>									
$C^{18}H^8O^2$ .....	132	....	100.00	.....	100.00	....	100.00	....	100.00

Mulder investigated the product (*a*) obtained by distillation from very old oil of cinnamon, and (*b*) that which was separated from the compound of nitric acid and cinnamic aldehyde.

*Decompositions.* 1. Cinnamic aldehyde absorbs moist *oxygen gas* rapidly, the dry gas more slowly, and is converted into cinnamic acid, without formation of any other product.



Oil of cinnamon thus treated always forms resin; but the oil separated from the compound of nitric acid and cinnamic aldehyde (considered by Mulder to be altered oil of cinnamon) is completely converted into white cinnamic acid by 24 hours' exposure to the air. (Mulder.)

When distilled in vessels containing air, it passes over of a pale yellow colour, becomes darker coloured in contact with the air, and on subsequent distillation with solution of salt, leaves a residue of cinnamic acid and resin. Very old oil of cinnamon which has become reddish brown, yields cinnamic aldehyde, when distilled with solution of salt (according to Mulder the product is altered oil of cinnamon), while cinnamic acid, and a mixture of 2 resins remains in the retort

2. Cinnamic aldehyde heated with *nitric acid* forms bitter almond oil and benzoic acid. (Dumas and Peligot.) Fuming nitric acid immediately changes a few drops of oil of cinnamon into a white crystalline mass, with disengagement of gas. Water then precipitates a small quantity of red resin, and separates hydride of benzoyl. One dram of oil of cassia mixed with fuming nitric acid becomes strongly heated, gives off gas, and forms a mixture of much resin and little unchanged oil, which after washing with water, dissolves with reddish brown colour in boiling alcohol. When the alcohol cools, brown flakes of  $\beta$ -resin precipitate, while  $\alpha$ -resin remains in solution. (Mulder.)

3. With *chromic acid*, cinnamic aldehyde forms benzoic and acetic acids. (Persoz.)

4. Boiled with solution of *hypochlorite of lime*, it forms benzoate of lime. (Dumas and Peligot.)

5. Oil of cinnamon distilled with *oil of vitriol* is completely decomposed, without forming benzoic acid. (Mulder.)

When oil of vitriol is dropped into oil of cinnamon, the oil acquires a fine colour, becomes warm, and thickens. If by the gradual addition of oil of vitriol the temperature be allowed to rise to  $50^\circ$ , but not higher, and if the liquids be well mixed and water added, the water takes up traces of cinnamic acid or benzoic acid, and leaves a brown resinous mass, from which, after washing out the sulphuric acid, alcohol dissolves  $\alpha$ -resin with reddish-brown colour, and leaves  $\beta$ -resin, which is soluble in ether. (Mulder.)

6. When oil of cinnamon is gradually heated in a *stream of chlorine*, the temperature being ultimately raised to the boiling point, heat is disengaged, the oil becomes brown, thickens, and is then decolorised, and the absorption ceases. If it be now heated, hydrochloric acid is liberated, and the oil distils over slowly in the stream of chlorine, leaving a considerable



black residue. The first part of the distillate is colourless and very mobile; yields, by long boiling with water, benzoic or cinnamic acid and hydrochloric acid, and with potash, chloride of potassium, and cinnamate or benzoate of potash; floats at first in oil of vitriol without alteration, but becomes changed in a few days into benzoic acid; absorbs ammonia and forms with it a solid mass, which dissolves in boiling water and crystallises in pearly needles on cooling. This portion of the distillate must therefore be regarded as a mixture of chloride of cinnamyl, hydrochlorate of cinnamic aldehyde, and quadrichloride of cinnamyl. — To the colourless distillate succeeds a yellow one. — If oil of cinnamon be completely saturated while warm with chlorine gas, quadrichloride of cinnamyl is formed. (Dumas and Peligot.)

7. When dry *hydrochloric acid gas* is passed for 24 hours through oil of cinnamon, the oil becomes green and solid. Water escapes with the hydrochloric acid, and if the residue be heated to  $80^{\circ}$  or  $100^{\circ}$ , more water is given off, and a small quantity of a peculiar, colourless oil, the greater part of which remains combined with the resin, and can only be expelled by stronger heat. The residue contains, besides this oil, a mixture of two resins combined with hydrochloric acid, from which water extracts hydrochloric acid, the green colour being thereby changed into dark brown. If all the hydrochloric acid be extracted with water, and the resin be then dissolved in boiling alcohol,  $\beta$ -resin precipitates in dark yellow flakes on cooling, and may be obtained pure by redissolving it in ether, while  $\alpha$ -resin remains in solution. (Mulder.) (See below.)

8. Cinnamic aldehyde is changed by *dry ammoniacal gas* into hydrocinnamide. (Laurent.) In contact with dry ammonia, it immediately absorbs a large quantity of gas, and becomes viscid (colours and thickens, Mulder); in 24 hours, the absorption is complete, and amounts to 12.3 parts of ammonia for 100 parts of oil. (Dumas and Peligot.) When 5.7 parts of ammonia are absorbed, the absorption ceases for a while, or altogether if the ammonia contains air (in 12 days, 11.56 parts of ammonia are taken up). The hard mass thus produced gives off much ammonia when treated with boiling water, the residue acquires a lemon-yellow colour, and an oil smelling like nutmeg is separated. If the residual resin be dissolved in boiling alcohol, yellow resinous flakes separate on cooling, the same resin remaining in solution combined with the oil, and separating as the oil volatilises. Hence it appears that oil of cinnamon is converted by ammonia into a compound of a resin with a peculiar volatile oil, from which boiling water expels ammonia. No cinnamic acid is formed at the same time. (Mulder.)

9. The alcoholic solution of cinnamic aldehyde is converted by *sulphide of ammonium* into thiocinnol. (Cahours.)

10. Fused with *hydrate of potash*, it gives off hydrogen and leaves a residue which appears to be cinnamic acid. To boiling potash-ley, oil of cinnamon gives up only the cinnamic acid which is already formed in it. (Dumas and Peligot.) Fixed alkalies produce from oil of cinnamon: hydride of benzoyl and benzoic acid, with elimination of carbon and hydrogen. Weak potash-ley forms with it a milk-white liquid, from which the oil does not separate. Strong potash-ley forms a brown liquid, from which water separates brown bitter almond-oil. When oil of cinnamon is distilled with strong potash-ley, hydrogen is evolved, carbon separated, and an oil passes over which is lighter than water, smells of oil of cinnamon and oil of bitter almonds, and contains 79.71 p. c. C, 7.45 H, and 12.84 O; but after three successive distillations with fresh potash-ley, it contains 81.6 p. c. C, 7.0 H, and 11.4 O; the residue yields a sublimate of benzoic acid when distilled with sulphuric acid. (Mulder.)



*Combinations; With Hydrochloric Acid;* Oil of cinnamon absorbs a large quantity of hydrochloric acid gas, acquiring a green colour and becoming thicker. If hydrochloric acid gas be passed into the liquid to saturation, 100 parts of oil take up 26.9 parts of hydrochloric acid. (Dumas and Peligot.) In contact with dry hydrochloric acid, it increases in weight by 19.85 to 20.82 per cent., though the oil evaporates in the hydrochloric acid gas. If the change of volume be determined in hydrochloric acid contained over mercury, it is found that 100 parts of oil take up 70 parts of gas, but the mercury becomes black, and likewise absorbs hydrochloric acid. (Mulder.)

					Dumas & Peligot.		Mulder.
$C^{18}H^8O^2$	.....	132	....	78.34	.....	78.8	.... 79.66
HCl	.....	36.5	....	21.66	.....	21.2	.... 20.34
<hr/>							
$C^{18}H^8O^2, HCl$	.....	168.5	....	100.00	.....	100.0	.... 100.00

*With Nitric Acid: Nitrate of Cinnamic Aldehyde; Nitrate of Oil of Cinnamon.* — Cinnamic aldehyde shaken up with concentrated nitric acid, combines with it, forming a crystalline mass. With commercial oil of cinnamon, large crystals are formed, but more slowly; they must be pressed between paper. (Dumas and Peligot.) (If oil of cinnamon be used, the paper takes up, besides nitric acid, a reddish-brown substance which may be extracted by perfectly absolute alcohol or ether, and is decolorised and decomposed by water. If the paper be exhausted with water, and the liquid neutralised with carbonate of soda and distilled, an oil passes over which has the odour of bitter almonds, contains 78.53 p. c. C, and 6.07 H, and by exposure to the air for 24 hours, is completely converted into benzoic acid. (Probably bitter almond-oil produced by the action of nitric acid on cinnamic aldehyde. Kr.) (Mulder.)

*Properties.* Transparent, oblique, rhombic prisms, often 2 or 3 inches long. (Dumas and Peligot.) Permanent in the air. (Mulder.)

					Dumas & Peligot.		Mulder. dried over sulphuric acid.
18 C	.....	108	....	58.06	.....	55.7	.... 57.16
N	.....	14	....	7.53	.....	6.8	.... 6.96
8 H	.....	8	....	4.30	.....	5.6	.... 4.90
7 O	.....	56	....	30.11	.....	31.9	.... 30.98
<hr/>							
$C^{18}H^8O^2, NO^5$	.....	186	....	100.00	.....	100.00	.... 100.00

According to Dumas and Peligot, it perhaps contains also an atom of water, which would require 55.38 p. c. C, 7.17 N, and 4.62 H.

*Decompositions.* 1. On preserving the compound, decomposition sets in, especially in a warm place, the mass becoming liquid and giving off nitrous gas, together with an odour of bitter almonds. (Dumas and Peligot.) The compound may be preserved in dry air, but decomposes in moist air, forming a red liquid which smells like bitter almonds. (Mulder.)

2. Water decomposes the compound, separating cinnamic aldehyde. (Dumas and Peligot.) The oil thus separated is considered by Mulder to be a product of decomposition different from the original oil. — 3. Cinnamic aldehyde dissolves in oil of vitriol with yellow colour; the addition of water renders the solution milky, and precipitates cinnamic acid. — 4. It dissolves in hydrochloric acid, and water separates from the solution a colourless oil. — 5. It is decomposed by aqueous ammonia, with separation of oil; ammoniacal gas forms, with disengagement of heat, a red resinous product, which is insoluble in water but soluble in alcohol. — 6. Concentrated potash-ley dissolves it, forming a reddish brown liquid, which is

decolorised by acetic acid. Weak potash-ley separates a yellow oil, (Mulder.)

Nitrate of cinnamic aldehyde is more soluble in boiling than in cold alcohol, and separates from the solution in granular crystals. It dissolves in ether. (Mulder.)

*With Bisulphite of Ammonia.*—Cinnamic aldehyde dissolves plentifully in aqueous bisulphite of ammonia, forming an oily liquid which afterwards solidifies to a crystalline magma. — Oil of cinnamon (from *cassia*) shaken up with a concentrated solution of bisulphite of ammonia, becomes heated and forms an emulsion, while oil-drops, not containing cinnamic aldehyde, separate on the surface, and the solution when strongly concentrated deposits crystals of the compound. (Bertagnini) With concentrated bisulphite of ammonia, oil of *cassia* soon solidifies to a yellow crystalline magma containing the substances which are mixed with cinnamic aldehyde in oil of *cassia*. By pressure, these can only be partially removed, and by recrystallisation only with loss of material and partial decomposition; they may, however, be removed by washing with alcohol of 80 or 90 per cent. (Gössmann.)

Even in closed vessels, the compound changes rapidly, and becomes dark brown. (Gössmann.) Distilled with hydrate of lime, it yields an aqueous ammoniacal distillate, and a dark yellow, or at a stronger heat, a dark brown oil, consisting of benzol and other hydrocarbons, cinnamic aldehyde, and triphenylamine (or bicinnamylamine. Kr.). (Gössmann.)

*With Bisulphite of Potash.*—Oil from Ceylon or Chinese cinnamon, shaken up with 3 or 4 times its volume of a solution of bisulphite of potash of 28° to 30° B. becomes heated and forms a solid, crystalline, scaly mass, which is freed from the mother-liquor, dried on a filter, powdered, washed with alcohol, as long as it passes through coloured and leaves a residue on evaporation, and then recrystallised from boiling alcohol.

Beautiful, silvery, intermingled plates. Nearly inodorous. Permanent in the air.

*Decompositions.* 1. When heated in a small tube, it gives off water, sulphurous acid, and cinnamic aldehyde, which in contact with the air is quickly converted into cinnamic acid. — 2. By heat or by the addition of acids, the aqueous solution is decomposed, giving off sulphurous acid and cinnamic aldehyde. The alcoholic solution is partially decomposed by boiling. — 3. In an aqueous solution, it is decomposed by *iodine* and by *bromine* without being coloured, and yields sulphuric acid and cinnamic aldehyde. Excess of bromine forms a solid substance having an aromatic odour, and fusible in warm water. — 4. When added to concentrated *nitric acid*, it is converted into sulphuric acid and nitrate of cinnamic aldehyde. — Dissolves in cold water. Insoluble in concentrated solutions of the alkaline sulphites. Dissolves sparingly in cold, readily in warm alcohol, and the solution solidifies to a crystalline mass on cooling. Insoluble in ether. (Bertagnini.)

*With Bisulphite of Soda.*—Oil of cinnamon becomes warm when heated with aqueous bisulphite of soda of 37° Bm., and immediately forms a fibrous crystalline mass, which, sometimes after a few minutes, sometimes after a longer period, becomes quite liquid, and forms two layers,—an upper oily layer, of smaller volume than the oil of cinnamon

(probably consisting of the volatile oils mixed with the cinnamic aldehyde, since it does not solidify either with alkaline bisulphite or with nitric acid), and a lower layer, which, on spontaneous evaporation, slowly deposits transparent crystalline nodules (probably the compound of cinnamic aldehyde with acid sulphite of soda) together with sulphate of soda. — The compound dissolves in boiling alcohol, separating out on cooling in long thin needles arranged in spherical groups. (Bertagnini.)

### Resins from Oil of Cinnamon.

MULDER. *J. pr. Chem.* 18, 385; *Ann. Pharm.* 34, 149.

#### 1. Resins formed in oil of cinnamon by the action of air.

*Preparation.* From the residue containing common salt, cinnamic acid, and two resins, which is left in the retort after distilling very old oil of cinnamon with solution of salt, cold water extracts the salt, and boiling water the cinnamic acid, leaving the resins. Boiling alcohol dissolves them, and on cooling deposits  $\beta$ -resin as a yellowish brown powder, and the rest is separated by repeated concentration and cooling of the reddish brown liquid. The residual solution leaves  $\alpha$ -resin on evaporation.

$\alpha$ -resin, easily soluble in cold alcohol.

Reddish-brown, transparent, very brittle. Melts at  $60^\circ$ .

Calculation according to Mulder.				Mulder.
30 C .....	180	...	79.29	78.33
15 H .....	15	...	6.61	6.49
4 O .....	32	...	14.10	15.18
<hr/>				
$C^{30}H^{15}O^4$ .....	227	...	100.00	100.00

The resin analysed had been kept for some hours in the melted state at  $100^\circ$ .

Decomposed by heated *nitric acid*. Dissolves at  $25^\circ$  in *oil of vitriol* with reddish brown colour; precipitated by water without decomposition. Does not dissolve in concentrated *hydrochloric acid* or in *ammonia*. Dissolves slowly in boiling *potash*.

Dissolves easily in cold alcohol with reddish brown colour, and is precipitated by acetic acid in yellow flakes. Dissolves easily and with red colour on ether, oil of turpentine, and olive-oil.

$\beta$ -resin, soluble only in hot alcohol.

Precipitated from the hot solution as a cinnamon brown powder. (It is formed on the cinnamon bark, and by its formation chiefly contributes to the colour of the bark.)

Lighter than water. Melts at  $145^\circ$  to a reddish brown resin, which, after being powdered, has the same properties as the unmelted resin.

Calculation according to Mulder.				Mulder. mean at $100^\circ$ .
12 C .....	72	...	84.71	83.45
5 H .....	5	...	5.88	6.06
O .....	8	...	9.41	10.49
<hr/>				
$C^{12}H O$ .....	85	...	100.00	100.00

Decolorised by warm *nitric acid*, with disengagement of gas. Dissolves in *oil of vitriol* with black colour, and is precipitated unchanged by water. Dissolves without change in boiling *hydrochloric acid*. Does not dissolve in *ammonia*, and scarcely in *potash*. The boiling alcoholic solution is not precipitated by boiling alcoholic solution of *sugar of lead*; on cooling, the resin separates free from lead.

Dissolves very little in cold, but readily in boiling alcohol, and in ether.

2. Resin formed when a dram of oil of cassia is added to fuming *nitric acid*. Preparation (p. 260). The resinous mass well exhausted with water and dissolved in hot alcohol, deposits on cooling, brown flakes of  $\beta$ -resin, while  $\alpha$ -resin remains dissolved with reddish-brown colour, and is obtained by evaporating the solution.

$\alpha$ -resin. Heavier than water.

Calculation according to Mulder.				Mulder.
18 C .....	108	....	69.68	..... 69.09
7 H .....	7	....	4.52	..... 4.44
5 O .....	40	....	25.80	..... 26.47
<hr/>				
$C^{18}H^7O^5$ .....	155	....	100.00	..... 100.00

It is not attacked by cold nitric acid, but is decomposed by the warm acid with disengagement of gas. Dissolves in cold oil of vitriol with reddish-brown colour. Does not dissolve in ammonia, but is soluble in potash with reddish brown colour, and is precipitated unchanged by sulphuric acid. Not precipitated from an alcoholic solution by sugar of lead. Dissolves in alcohol and ether.

3. Resins produced by *oil of vitriol*. (p. 260.)

$\alpha$ -resin soluble in alcohol.

Freed from  $\beta$ -resin by re-solution in cold alcohol.

Reddish brown, slightly transparent. Melts at  $90^\circ$ .

Calculation according to Mulder.				Mulder. <i>melted at <math>100^\circ</math>.</i>
30 C .....	180	....	85.31	..... 84.38
15 H .....	15	....	7.11	..... 7.26
2 O .....	16	....	7.58	..... 8.36
<hr/>				
$C^{30}H^{15}O^2$ .....	211	....	100.00	..... 100.00

Decomposed with difficulty by boiling *nitric acid*. Dissolves in warm *oil of vitriol*, with beautiful violet colour; precipitated colourless by water. Does not dissolve in boiling *hydrochloric acid*, ammonia, or in potash. Dissolves in cold alcohol, and in ether with reddish brown colour; in oil of turpentine, and in olive-oil with red colour.

$\beta$ -resin  $C^{30}H^{15}O^2$ , insoluble in alcohol. Infusible at  $300^\circ$ . Contains, according to Mulder's analysis, 87.33 p. c. C., 7.23 H., and 5.44 O.—Dissolves with blue-violet colour in gently heated *oil of vitriol*. Boiling nitric acid decomposes without dissolving it. Insoluble in boiling *hydrochloric acid*, also in ammonia and potash. Insoluble in boiling alcohol, easily soluble in cold ether. Dissolves with red colour in oil of turpentine and olive-oil.

4. Resins produced by *hydrochloric acid*. (p. 261.)

$\alpha$ -resin. Freed from adherent oil by being heated to  $140^\circ$ , as long as any odour is disengaged.

Beautiful reddish brown, transparent, brittle; melts at  $85^\circ$ .

Calculation according to Mulder.				Mulder.
14 C .....	84	...	85.71	84.58
6 H .....	6	...	6.12	6.25
O .....	8	...	8.17	9.17
<hr/>				
$C^{14}H^6O$ .....	98	...	100.00	100.00

Boiling *nitric acid* decomposes it, with production of a yellow colour. Cold *oil of vitriol* dissolves it with violet-red, or at a gentle heat with blood-red colour. Insoluble in boiling *hydrochloric acid*; also in ammonia, and in potash. Dissolves easily in cold alcohol and ether. Dissolves with blood-red colour in oil of turpentine, and in olive-oil.

$\beta$ -resin. Freed from adherent oil by being heated to  $140^\circ$ . Red-brown powder, becoming dark brown after solution in ether and evaporation; and after being heated to  $140^\circ$ , dark brown, lustrous like sulphide of molybdenum. Melts at  $160^\circ$ .

Calculation according to Mulder.				Mulder. dried at $140^\circ$ . mean.
20 C .....	120	...	88.23	87.25
8 H .....	8	...	5.88	5.72
O .....	8	...	5.89	7.03
<hr/>				
$C^{20}H^8O$ .....	136	...	100.00	100.00

Warm *nitric acid* decomposes without previously dissolving it. Dissolved by *oil of vitriol* at  $50^\circ$  with reddish brown colour. Neither dissolved nor changed by boiling *hydrochloric acid*, by ammonia, or by potash. Does not dissolve in cold, and but little in boiling alcohol, and is deposited as a dark yellow powder on cooling. Dissolves readily in ether, with reddish brown, in oil of turpentine and in olive-oil with brown colour.

5. Resin formed by *ammonia*. (p. 261.) Deposited from alcohol in yellow flakes. Melts at  $150^\circ$  to a reddish brown mass. Is similar to, but not identical with, the  $\beta$ -resin; formed by the action of the air on oil of cinnamon.

Calculation according to Mulder.				Mulder. mean.
14 C .....	84	...	85.71	84.74
6 H .....	6	...	6.12	5.87
O .....	8	...	8.17	9.39
<hr/>				
$C^{14}H^6O$ .....	98	...	100.00	100.00

It has therefore the same composition as the  $\beta$ -resin produced by *hydrochloric acid*.

Cold *nitric acid* does not dissolve it; the boiling acid colours it red, and dissolves it, with disengagement of gas, and forms a yellow liquid. Dissolves in *oil of vitriol* with bright brown colour, and is precipitated

by water unchanged. Boiling *hydrochloric acid* colours it dark brown without dissolving it. Dissolves, but is not changed by boiling ammonia and potash. Insoluble in cold, but soluble in boiling alcohol. Dissolves in ether.

### Compound of Iodine, Iodide of Potassium, and Oil of Cinnamon.

APJOHN. (1838.) *Lond. Ed. Mag. J.* 13, 113; *J. pr. Chem.* 15, 168; *Ann. Pharm.* 28, 314.

DESPAN. *J. Pharm.* 26, 207.

OSWALD. *N. Br. Arch.* 170, 149; *Pharm. Centr.* 1852, 924.

*Formation and Preparation.* A gallon of cinnamon-water, which has been distilled from 1 pound of cassia-cinnamon and 2 gallons of water, is cooled, and 4 ounces of iodide of potassium and 40 grains of iodine are added. The mixture becomes immediately turbid, and gives a yellowish precipitate, which quickly becomes crystalline. The liquid, which contains no more oil of cinnamon or iodine, is decanted; and the crystals are thrown on a filter, drained, and laid on a piece of chalk, where they soon dry, the liquid being absorbed. 60 grains are obtained (a temperature of 0° is necessary for success); at 4°—5° only a small quantity of a brown powder is obtained, which only becomes crystalline in the cold. (Apjohn.)

Despan takes for 1 part of iodine, 26 parts of iodide of potassium and 1860 parts of cinnamon-water, and collects the crystals separated after 12 hours. Oswald dissolves 2 grains of iodine and 1 dram of iodide of potassium in 3 ounces of cinnamon-water, and obtains 1 grain of crystals. With less iodide of potassium, oil separates, which becomes crystalline by contact with iodide of potassium. The solution of oil of cinnamon in a little alcohol yields, when mixed with iodine, iodide of potassium, and water, nothing but oil, no crystals. (Oswald.)

*Properties.* Golden yellow or brown four-sided needles having a metallic lustre. Has a burning and biting taste, like oil of cinnamon and at the same time like iodine (Apjohn); sweetish (Despan); and like cinnamon. (Oswald). Smells of cinnamon. (Despan, Oswald.) Melts at 28° (Apjohn), at a very low temperature (Despan, Oswald), to a dark liquid, and solidifies unchanged on cooling. (Apjohn, Despan.) On paper at 10°, it evaporates completely in 24 hours.

Calculation according to Apjohn.				Apjohn.
KI	.....	166.2	.... 12.43	..... 12.55
3 I	.....	381	.... 28.33	..... 28.14
108 C	.....	648	.... 48.36	..... 49.62
48 H	.....	48	.... 3.58	..... 4.07
12 O	.....	96	.... 7.30	..... 5.62
KI, 3I, 6(C <sup>18</sup> H <sup>8</sup> O <sup>2</sup> )				..... 100.00
		1339.2	.... 100.00	..... 100.00

The compound perhaps contains the iodide of potassium merely adhering, since, according to Despan, it is quite volatile. Apjohn formerly found more iodine.

*Decompositions.* 1. Burns on platinum foil with the odour of cinnamon, and then of iodine, and leaves a small quantity of charcoal which ultimately burns away. (Despan.)

2. Heated above the melting point, it gives off iodine vapours with the odour of oil of cinnamon, and leaves charcoal and iodide of potassium. (Apjohn.)

When distilled, it gives off brownish red vapours, which condense on the upper part of the retort to blackish red drops, and afterwards violet vapours; a dark red oil passes over, which smells of cinnamon, and tastes sweet, while a little charcoal remains. (Despan.)

3. Water decomposes the compound, extracting iodide of potassium, and separating black oil-drops. (Apjohn, Despan.) Water at  $0^\circ$  acts more slowly, and if it contains iodide of potassium, does not decompose the compound. (Apjohn.)

4. Decomposed by potash, with formation of iodide of potassium, iodate of potash, and free oil of cinnamon. If the crystals are distilled with an atom of dilute ley, cinnamon-water passes over, which no longer produces crystals with iodine and iodide of potassium, has an odour somewhat different from that of cinnamon-water, and reddens litmus. (Apjohn.)

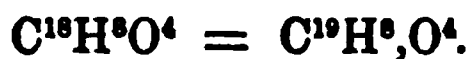
5. When dissolved in water, alcohol, or ether, it is decomposed by zinc, iron filings, or mercury, yielding iodide of the metal and oil of cinnamon. (Apjohn.)

*Combinations.* Dissolves easily in cold water. (Oswald.) (See above.)

Its aqueous solution is precipitated white by ammonia. (Oswald.)

Dissolves easily in alcohol, and ether, crystallising out unchanged on spontaneous evaporation. These solutions colour starch blue (Apjohn), reddish brown (Oswald).

### Cinnamic Acid.



DUMAS & PELIGOT. *Ann. Chim. Phys.* 57, 305; *J. pr. Chem.* 3, 57; *Ann. Pharm.* 14, 86.

MULDER. *Pogg.* 41, 398; *J. pr. Chem.* 18, 253 and 391; *Ann. Pharm.* 34, 371; *J. pr. Chem.* 19, 363.

PLANTAMOUR. *Ann. Pharm.* 30, 341.

MARCHAND. *J. pr. Chem.* 16, 60; 18, 253.

C. SIMON. *Ann. Pharm.* 31, 265; *N. Br. Arch.* 29, 182.

ERDMANN & MARCHAND. *J. pr. Chem.* 17, 176.

FREMY. *Compt. rend.* 7, 250; *J. pr. Chem.* 16, 59; *Ann. Chim. Phys.* 70, 187; *J. pr. Chem.* 18, 230; *Ann. Pharm.* 30, 330.

HERZOG. *N. Br. Arch.* 20, 159; 23, 17; *J. pr. Chem.* 29, 51.

MITSCHERLICH. *J. pr. Chem.* 22, 192; *N. Ann. Chim. Phys.* 4, 73; 7, 5.

DUMAS & STASS. *N. Ann. Chim. Phys.* 1, 53.

STENHOUSE. *Phil. Mag. J.* 19, 38; *J. pr. Chem.* 26, 126; *Phil. Mag. J.* 27, 130; *Ann. Pharm.* 55, 3; *Ann. Pharm.* 57, 79; *Phil. Mag. J.* 27, 366; *J. pr. Chem.* 37, 288.



E. KOPP. *Compt. rend.* 21, 1376; *J. pr. Chem.* 27, 280; *Compt. rend.* 24, 614; *N. J. Pharm.* 11, 426; *J. pr. Chem.* 41, 425; *Compt. chim.* 1849, 146; 1850, 140.

HEMPEL. *Ann. Pharm.* 59, 316.

CAHOURS. *Compt. rend.* 22, 846; *Ann. Pharm.* 60, 254; *N. Ann. Chim. Phys.* 23, 341; *J. pr. Chem.* 45, 140; *Ann. Pharm.* 70, 42.

SCHABUS. *Wien. Akad. Ber.* 1850, 2, 206.

CHIOZZA. *N. Ann. Chim. Phys.* 39, 439; *J. pr. Chem.* 61, 235; *Ann. Pharm.* 86, 264.

J. LÖWE. *J. pr. Chem.* 66, 188.

PIRIA. *Ann. Pharm.* 100, 104.

BERTAGNINI. *Nuovo Oimento* 4, 46; *Ann. Pharm.* 100, 125.

*Zimmtsäure, Cinnamylsäure, Acide cinnamique.*

Trommsdorff (*Alm.* 1780, 17) first mentions that water distilled off cinnamon, deposits after standing for half a year, crystallised cinnamon-salt. Dumesnil (1817, *Schw.* 21, 224), Henkel (*Repert.* 4, 383), Buchner (*Repert.* 6, 1; 8, 184), and Bollaert (*Quart. J. of Sc.* 18, 319) observed the separation of solid crystalline masses from oil of cinnamon, which they took for benzoic acid, while Turner considered them to be camphor, and Boullay (*J. Pharm.* 14, 499) regarded them as identical with or similar to the crystals from oil of cloves. Bizio (*Brugn. Biorn.* 19, 364) showed that the acid produced in oil of cinnamon is different from benzoic acid, on the ground of its behaviour with nitric acid and oil of vitriol; but Dumas and Peligot in 1834 first demonstrated its individuality and established its composition, whereupon also the acid in Peru and Tolu balsam and in liquid storax, which Bonastre, Herberger (*Repert.* 55, 210) and Simon had taken for benzoic acid, was recognised by Buchner (*Repert.* 55, 210), Fremy, Plantamour, and Marchand as cinnamic acid. The cinnamates were principally investigated by Herzog in 1839, who also first prepared cinnamic ether.

*Sources.* The acid separates from cinnamon-water when left to itself. (Trommsdorff, Stookmann *N. Tr.* 14, 237, Dumas & Peligot.) From oil of cinnamon in the same manner. (Dumesnil, Hennel, Buchner, Bizio, Boullay, Dumas, & Peligot.)

It is also found in the deposit from Peru balsam (Herberger), in the balsam itself, and in Tolu balsam. (Fremy, Plantamour.) In liquid storax. (Bonastre, Simon, Erdmann, & Marchand.)

*Formation.* 1. Cinnamic aldehyde becomes oxidised to cinnamic acid, when exposed to the air or to oxygen (Dumas & Peligot), a resin being formed at the same time. (Mulder.) 2. — Styrene is changed into cinnamic acid by oxidising agents. 3. — Equal quantities of oil of bitter almonds, and chloride of acetyl heated in a sealed tube for 20—24 hours at 120°—130° (at 200°, secondary products would be formed) yield hydrochloric acid and cinnamic acid, which may be extracted from the viscid residue by ammoniacal water. (Bertagnini.) — 4. Cinnamein is decomposed by boiling with concentrated potash-ley, into cinamate of potash, and peruvine (p. 285). (Fremy, Plantamour.) — 5. Styracin is changed by melting potash, with liberation of hydrogen, into cinamate of potash (Fremy); by boiling with potash-ley it is changed into cinamate of potash and styrene. (Simon.)

*Preparation.* I. From the deposit of cinamate of lead, mixed with



cinnamic acid, resin, and oil of cinnamon, found in the old leaden original packages, in which oil of cassia-cinnamon is imported. — The deposit is dissolved in alcohol, and filtered from the cinnamate of lead, and the alcohol is removed from the filtrate by distillation; the cinnamic acid then quickly crystallises out from the oil, and is purified by treatment with carbonate of soda and precipitation. The residual cinnamate of lead is boiled with carbonate of soda, filtered from the carbonate of lead, and the cinnamic acid is precipitated by dilute sulphuric acid, in silvery lustrous laminæ, which are washed, and recrystallised from alcohol. (Herzog.) Dumas & Peligot dissolve the crystalline deposit from oil of cinnamon in boiling water, and evaporate the filtrate to the crystallising point.

II. *From liquid Storax.* — Liquid storax is distilled with water and one-half to seven-tenth parts of crystallised carbonate of soda, whereupon styrol passes over. The residual aqueous liquid is filtered from the resin; and the filtrate is mixed at first with just so much sulphuric acid, that a very little cinnamic acid is precipitated along with dissolved resin; and the liquid filtered from this precipitate is treated with excess of sulphuric acid, which precipitates cinnamic acid of a tolerably white colour. It is dissolved in a large quantity of water, with as little carbonate of soda as possible, and again precipitated, first with a little sulphuric acid, and then, after the filtration, with an excess of acid, by which a white precipitate is formed. This is washed with water, dried, and dissolved in alcohol, which, by spontaneous evaporation, yields quite white and very large crystals. (E. Simon.) Erdmann and Marchand purify the acid by distillation, pressure between paper moistened with alcohol, and repeated crystallisation. Herzog boils liquid storax for an hour with two parts of water, and so much potash, that a distinct alkaline reaction is manifest; dilutes with water; allows it to settle; washes the residue a few times with water; strains the whole through linen; mixes it with dilute sulphuric acid, as long as turbidity is produced; boils it strongly in a tin vessel; and filters hot, whereupon resin remains, and cinnamic acid crystallises out on cooling. This product is collected on a filter, washed with water, and recrystallised, first from boiling water, and then from alcohol. (The product varies very much. A pound of storax gives from 6 drams to an ounce of acid; the residual storax, when again boiled with alkaline water, yields but very little acid.) (Herzog.) Hempel also boils the storax with excess of potash-ley, since an alkaline carbonate does not fully exhaust it. Like Simon, he first precipitates the resin, together with a little cinnamic acid, and then throws down the purer cinnamic acid by an excess of hydrochloric acid. In this way, 1 pound of storax yields 2 ounces of cinnamic acid.

Löwe pours concentrated solution of carbonate of soda on liquid storax; adds a sufficient quantity of hydrate of lime; boils for eight hours, replacing the water which evaporates; decants; washes the residue; repeats this operation four times; precipitates the united liquors with hydrochloric acid; dissolves the precipitate in carbonate of soda; again precipitates with hydrochloric acid; and thus obtains seven ounces and a half of dry cinnamic acid from 2 pounds of storax.

III. *From Balsam of Peru.* — When the slimy residue which deposits in Peruvian balsam, by keeping, is dissolved in warm alcohol, and the filtrate is placed in a tall and narrow cylinder with a layer of water on

the top, crystals of nearly pure cinnamic acid separate in a few days from the clear brown liquid. (Herberger.) Peruvian balsam is boiled with thick milk of lime; the liquid filtered; the residual magma exhausted three or four times with boiling water; and the solution again filtered. On the filter there remains a resin to which cinnamein tenaciously adheres. The filtrate deposits on cooling, loose, almost white masses of crystals; and these, when decomposed by hydrochloric acid, yield nearly pure cinnamic acid, which may be obtained perfectly pure, either by distillation, or by solution in ammonia, filtration, and precipitation while hot by hydrochloric acid. (E. Kopp.) Simon proceeds as with storax.

IV. *From Balsam of Tolu.* — Balsam of Tolu is boiled six or seven times with solutions of carbonate of soda which are taken continually weaker (the last extracts alone contain a little benzoic acid, produced by the action of the alkali on the resin); and the alkaline decoctions are strongly concentrated by evaporation, and precipitated hot by hydrochloric acid, whereupon most of the cinnamic acid melts into a brown resin, and but little crystallises out on cooling. The latter is pressed, the resin is pulverised, and both are dissolved in ammonia diluted with 2 parts of water, and heated to 80°. The greater part of the resin then remains dissolved. The liquid is filtered; the residue is boiled with water; and the whole of the very brown liquids are evaporated and decomposed, while boiling, by hydrochloric acid, whereupon most of the acid again melts, while the remainder separates out on cooling in nearly white crystalline scales, which are pressed, and washed with a little cold water. The melted acid is also washed with a little water. The whole of the acid is heated in a porcelain dish covered with paper till the water is expelled — very little acid subliming even at 200° — and the fused residue is bruised and distilled. Pure cinnamic acid then passes over as a colourless, clear, strongly refracting liquid, which solidifies to a white crystalline mass like stearin. Towards the end, yellowish vapours arise, which, when collected in another receiver, solidify to a mass of acid, which is contaminated by the presence of the empyreumatic oils of the resin, but may be obtained quite pure by recrystallisation from boiling water. (E. Kopp.)

*Properties.* Crystallises from alcohol in colourless prisms belonging to the oblique prismatic system, like gypsum. Cleavage paralld to the terminal face of the second lateral axis.  $\infty a : b : \infty c$  and semi-octohedral face :  $\frac{1}{2} (a : b : c)$  with a more obtuse angle than the prism of the principal axis. The principal dimension is the direction of the first secondary axis :  $a$ . — Crystallises from water in the same system with the same laminated fracture; the direction of the second lateral axis is but very slightly developed, so that rhombic tables are thereby formed. (Herzog.) Crystallises in transparent, six-sided prisms with two broader faces (Buchner, Stookmann); by spontaneous evaporation from alcohol in beautiful, flat, oblique prisms with rectangular base. (E. Kopp.) Colourless, pearly laminæ. (Dumas & Peligot.) Acute rectangular prisms, acuminate by truncation of the similar edges of the base. Crystallises from concentrated solutions in tolerably long needles with indistinct faces. (Wackenroder.) — Fig. 87 without  $i$  and  $h$ .  $a : t = 107^\circ 23'$ ;  $a : u = 106^\circ 25'$ ;  $a : u$  behind  $= 96^\circ 2'$ ;  $u' : u = 99^\circ 6'$ ;  $u : u'$  behind  $80^\circ 54'$ ;  $u : t = 130^\circ 27'$ . Cleavage parallel to  $t$ . Lustre resinous, nacreous on  $t$ . (Schabus, *Wien. Akad. Ber.* 1850, 2, 206.)  $u' : u = 98^\circ 44'$  and  $97'$ ,  $a : a = 146^\circ$ . (G. Rose, *Ann. Pharm.* 31, 269.)

Melts when heated (Bizio), at  $120^\circ$  (Dumas and Peligot), at  $137^\circ$  (Herzog), at  $129^\circ$  (E. Kopp), to an oil, which solidifies at  $135^\circ$  (Herzog), to a buttery mass. (Dumesnil.) Boils at  $293^\circ$  under 0.765 met. pressure (Dumas and Peligot), at  $290^\circ$  (Herzog), at  $300^\circ - 304^\circ$  (E. Kopp) and volatilises quite unchanged in suffocating vapours which excite coughing. (Dumas & Peligot.) May be sublimed at a gentle heat in lustrous laminæ. (When melted on paper it leaves grease-spots.) (Henkel.) Sp. gr. 1.195 (Schabus); 1.245. (E. Kopp.) Inodorous (Bizio, Herzog); smells feebly of cinnamon (Dumesnil, Buchner); aromatic. (Schabus.) Tough like gypsum. (Dumesnil.) Tasteless (Bizio); tastes feebly of cinnamon (Buchner), neither acid nor alkaline (Dumesnil); sweetish, burning and suffocating (Tromsdorff, Henkel, Herberger); at first not at all, and then very slightly grating. (Schabus.) Reddens litmus.

			Dumas & Peligot.	Mulder.	Fremy.	Herzog.
			mean.	mean.		
18 C	108	...	72.97	72.43	72.58	72.39
8 H	8	...	5.41	5.67	5.64	5.59
4 O	32	...	21.62	21.90	21.78	22.02
$C^{18}H^8O^4$	148	...	100.00	100.00	100.00	100.00

	Erdmann & Marchand.	Cahours.	E. Kopp.
	dried in vacuo at $100^\circ$		distilled and remelted.
18 C	72.93	72.73	72.94
8 H	5.43	5.46	5.36
4 O	21.64	21.81	21.70
$C^{18}H^8O^4$	100.00	100.00	100.00

Dumas & Peligot analysed the acid from oil of cinnamon; Fremy that from cinnamein; Erdmann & Marchand, the acid from liquid storax; E. Kopp, that from balsam of Tolu.

*Decompositions.* 1. Every time the acid is distilled, a trace of an odorous oily substance is formed; but the acid freed from this substance by crystallisation from alcohol, experiences no change by distillation. (Fremy.) — 2. Placed on red-hot platinum-foil, or held in the flame of a candle, cinnamic acid burns with fuliginous flame. (Henkel, Bizio, Herberger, Herzog). On red-hot charcoal, it evaporates without flame with a strong biting smoke. (Henkel.) — 3. Cold oil of vitriol colours the acid yellow, and then dissolves it, with evolution of heat, forming a clear, brownish liquid, which on addition of water, deposits a very small quantity of a brownish white powder. Anhydrous sulphuric acid immediately decomposes the acid, with separation of charcoal, and evolution of a vapour resembling benzoin. In both cases, sulphocinnamic acid is formed. — 4. Cinnamic acid heated with excess of iodine melts to a dark brown mass; and when this mass is heated with water, and the excess of iodine expelled by evaporation, iodocinnamic acid crystallises out on cooling. (Herzog.) — 5. Bromine passed over cinnamate of silver forms bromocinnamic acid. (Herzog.) — 6. Chlorine passed in diffused daylight over dry cinnamic acid, forms a tough greasy substance, which, when heated with carbonate of potash, forms chlorobenzoate (chlorocinnamate; Herzog) of potash, and deposits a white oil containing chlorine. (Herzog.) The same products are formed when chlorine is passed into warm aqueous cinnamic acid, and when cinnamic acid is distilled with

hypochlorite of lime (Stenhouse), or with chlorate of potash and hydrochloric acid. (Hofmann.) On passing chlorine into a solution of cinnamic acid in concentrated carbonate of soda, chlorocinnamic acid is formed, and when heat is employed, violent action ensues, and Stenhouse's chlorinated oil is formed, together with chlorobenzoic acid. (E. Kopp.) Hypochlorite of lime converts cinnamic acid into oil of bitter almonds, and then into benzoate of lime. Formic acid appears also to be one of the products of the reaction: for the liquid, if mixed after neutralisation, with nitrate of silver or mercuric nitrate, deposits a considerable quantity of metallic silver or mercury. (Dumas & Peligot.)—7. Strong *nitric acid* easily dissolves cinnamic acid; below 60°, without disengagement of gas, it forms nitrocinnamic acid, which then crystallises (Mitscherlich, Kopp); at a higher temperature (or by the spontaneous rise of temperature produced when more than 1 part of cinnamic acid is taken to 8 parts of nitric acid) the nitric acid is violently reduced to nitric oxide, and nitrobenzoic acid is formed (Mitscherlich); or, according to Kopp, first benzoic, and then nitrobenzoic acid. With a more dilute acid, hydride of benzoyl is first produced (Dumas & Peligot, Mulder, Herzog, Plantamour, Simon), then benzoic acid (Dumas & Peligot, Herzog, Simon, Mulder); nitrobenzoic acid contaminated by a yellow substance (Plantamour, Mulder). By distilling cinnamic acid with fuming nitric acid, Simon obtained hydride of benzoyl, and a residue of benzoic acid, picric acid and resin. The distillate was at first free from hydrocyanic acid, but contained that acid after rectification over common salt.

8. Boiled with *peroxide of lead* in aqueous solution, cinnamic acid gives off the odour of bitter almond oil, while the peroxide of lead assumes a light yellow colour, and is partially converted into benzoate of lead. This behaviour serves to distinguish cinnamic acid from benzoic acid. (Stenhouse.)—9. Cinnamic acid distilled with sulphuric acid and *bichromate of potash* yields oil of bitter almonds. (Simon.) The odour of bitter almond oil is produced, even in the cold. (Kopp.)—10. With *penta-chloride of phosphorus* (also with the terchloride, according to Bechamp) it yields chloride of cinnamyl. (Cahours.)—11. Fused with *hydrate of potash*, it gives off hydrogen, and forms acetate and benzoate of potash, together with a little salicylate of potash produced by the action of potash on the benzoic acid previously formed. (Chiozza):



Cinnamic acid is not decomposed by boiling with strong caustic potash. (Simon.)

12. In the dry distillation of the alkaline cinnamates or of cinnamic acid with *caustic baryta* or lime, a carbonate is formed, together with cinnamene and benzol. (Compare xiii, 3.)

13. Cinnamate of *lime* distilled with *formiate of lime* yields cinnamic aldehyde. (Piria.)

The reactions 6, 7, and 8, serve to distinguish cinnamic acid from benzoic acid.

**Combinations.** Cinnamic acid dissolves very sparingly in cold, easily in boiling water. — The aqueous solution may be continuously boiled, without production of benzoic acid. (Dumas and Peligot.)

**Cinnamates.** — The cinnamates are soluble in water and crystallisable; they strongly resemble the salts of benzoic acid. (Dumas & Peligot.) The silver-salt is the least soluble. Those which are difficultly soluble,

dissolve more readily in water containing chlorides or nitrates. From almost all solutions of these salts the cinnamic acid is precipitated by acids. They are decomposed by dry distillation, giving off the odour of bitter almonds. With concentrated nitric acid, they turn yellow, and give off the odour of oil of cinnamon and bitter almond oil. Oil of vitriol colours them brown. The solutions mixed with manganous salts, in such proportion that the cinnamate predominates, give a white precipitate, which soon becomes yellowish and crystalline. (Benzoates give no precipitate.) With ferrio salts they form a yellow, not a reddish precipitate. (Herzog.)

*Cinnamate of Ammonia.* —  $C^{18}H^7O^3, NH^4O$ . — When cinnamic acid is dissolved in warm aqueous ammonia, the liquid solidifies to a crystalline mass on cooling. The mother-liquor is poured off, and the salt dried between bibulous paper at the ordinary temperature. Crystals belonging to the oblique prismatic system, with laminated fracture parallel to the terminal face of the second lateral axis, secondly to the oblique terminal face of the principal axis, and thirdly (but less distinct) to the posterior acute terminal face. Direction of the principal axis most strongly developed, that of the two secondary axes (which? Gm.) very little. Colourless, inodorous; has a biting taste, with grating after-taste. Permanent in the air.

In hot air it gives off ammonia.

When heated in a glass tube, it melts, evolves ammonia, yields a sublimate of small strongly iridescent crystals, probably an amidogen-compound, and leaves a light brown resin.

Sparingly soluble in cold, easily in hot water; on boiling the solution an acid salt is formed, with disengagement of ammonia. (Herzog.)

*Cinnamate of Potash.* — Cinnamic acid is added to boiling potash-ley till acid reaction is set up, and the liquid is then evaporated to crystallisation. At first the sparingly soluble acid salt crystallises out, and then the more easily soluble neutral salt. — *Neutral.* — Crystallises like the ammonia-salt. Permanent in the air. Heated in a glass tube, it melts and gives off an atom of water at  $120^\circ$ , but bears a stronger heat without decomposition. Dissolves easily in hot water. (Herzog.)

					Herzog.
KO .....	47.2	...	24.18	.....	23.72
$C^{18}H^8O^4$ .....	148	...	75.08		
<hr/>					
$C^{18}H^7KO^4 + Aq$ ...	195.2	...	100.00		

*Cinnamate of Soda.* — Carbonate of soda is saturated with cinnamic acid, and evaporated to the crystallising point. Dull crystals belonging to the oblique prismatic system, exhibiting an indistinct cleavage parallel to the right terminal face of the second lateral axis. The faces are but indistinctly developed, excepting the right terminal face of the first lateral axis, and the anterior oblique terminal face. Principal axis predominating. At  $110^\circ$  the salt gives off 1 At. water. (Herzog.)

					Herzog.
NaO .....	31	...	17.31	.....	17.05
$C^{18}H^8O^4$ .....	148	...	82.69		
<hr/>					
$C^{18}H^7NaO^4, Aq$ ...	179	...	100.00		

*Cinnamate of Baryta.* — Chloride of barium is precipitated by cinnamate of ammonia: White precipitate which in sunlight changes into beautiful, strongly refracting crystals. Crystals belonging to the oblique prismatic system, with cleavage parallel to the right terminal face of the second lateral axis. At 100° it gives off 7.15 per cent. water. Dissolves with difficulty in cold, readily in boiling water, from which it crystallises.

<i>Crystals.</i>				<i>Herzog.</i>
BaO .....	76.6	...	32.79	
C <sup>18</sup> H <sup>7</sup> O <sup>3</sup> .....	139	...	59.51	
2HO .....	18	...	7.70	7.15
<hr/>				
C <sup>18</sup> H <sup>7</sup> BaO <sup>4</sup> , 2Aq ....	233.6	...	100.00	

<i>At 100°.</i>				<i>Herzog.</i>
BaO .....	76.6	...	35.53	35.16
C <sup>18</sup> H <sup>7</sup> O <sup>3</sup> .....	139	...	64.47	
<hr/>				
C <sup>18</sup> H <sup>7</sup> BaO <sup>4</sup> .....	215.6	...	100.00	

*Cinnamate of Strontia.* — Prepared like the baryta-salt, which it resembles in properties and in crystalline form. (Herzog.)

*Cinnamate of Lime.* — 1. Lime-water precipitates small needles from moderately concentrated cinnamate of ammonia. — 2. Nitrate of lime produces in solutions of cinnamate of ammonia, a white precipitate, which is obtained in the crystalline form on cooling from a solution in boiling water. Crystals belonging to the oblique prismatic system, with cleavage parallel to the right terminal face of the second lateral axis. (White, loosely coherent crystalline mass or aggregated nodules: E. Kopp.) Gives off water at 110° (Herzog); the greater part at 140°. (E. Kopp.) Dissolves with difficulty in cold water (Herzog), less easily than benzoate of lime. (E. Kopp.)

<i>Crystals.</i>				<i>Herzog.</i>
CaO .....	28	...	15.14	15.20
C <sup>18</sup> H <sup>7</sup> O <sup>3</sup> .....	139	...	75.13	
2HO .....	18	...	9.73	9.77
<hr/>				
C <sup>18</sup> H <sup>7</sup> O <sup>3</sup> , CaO, + 2Aq ....	185	...	100.00	

Hempel could not detect cinnamene among the distillation-products of cinnamate of lime, but thinks it might be formed by very careful heating till decomposition sets in.

*Cinnamate of Magnesia.* — When magnesia alba is heated with alcoholic cinnamic acid, solution takes place with effervescence, and the compound crystallises out on cooling. Crystals belonging to the oblique prismatic system, with cleavage like that of cinnamate of lime. The lateral axis is almost as strongly developed as the principal axis. (Herzog.)

*Cerous and Lanthanous Cinnamate.* — Precipitated as granular powders. (Herzog.)

*Cinnamate of Glucina and Cinnamate of Alumina.* — Loose, white



powders sparingly soluble in cold, easily soluble in hot water. (Herzog.)

With *uranous* salts alkaline cinnamates form a yellowish precipitate soluble in hot water. (Herzog.)

*Manganous Cinnamate*. — Even dilute solutions of chloride of manganese are precipitated by alkaline cinnamates. The precipitate, at first white, soon becomes yellowish and crystalline. The salt crystallises from a hot solution in golden yellow cleaveable crystals belonging to the oblique prismatic system. Dissolves with difficulty in cold, and slowly in hot water. (Herzog.)

*Antimonious Cinnamate*. — The precipitated as well as the ignited oxide of antimony, dissolves with difficulty in cinnamic acid. Tartar-emetic gives with alkaline cinnamates, after some time, small needles grouped in reticulated masses, which partially disappear again by longer contact with the liquid; when collected on the filter and dried, they form a silvery coating. They contain water, melt when heated, and leave a colourless residue which effervesces with acids, gives an orange-coloured precipitate with sulphuretted hydrogen, and is therefore probably a double salt with potash. (Herzog.)

Alkaline cinnamates precipitate *bismuth*-salts white, and form in solutions of oxide of tin, a white curdy precipitate. (Herzog.)

*Cinnamate of Zinc*. — Zinc dissolves with difficulty in hot aqueous cinnamic acid, with liberation of hydrogen. A solution of oxide of zinc in cinnamic acid crystallises on evaporation. Crystals like those of the lime-salt. Dissolves with tolerable facility in water. (Herzog.)

*Cinnamate of Cadmium* resembles the zinc-salt. (Herzog.)

*Cinnamate of Lead*. — 1. Solution of neutral acetate of lead is precipitated at the boiling temperature by cinnamate of potash, and the white crystalline precipitate is well washed with water. — 2. Cinnamic acid is continuously boiled with a great excess of neutral acetate of lead, and evaporated, a large quantity of acetic acid then escaping; and the gelatinous mass is again diluted with water, the solution filtered, and the residue washed for some time with water, and at last with alcohol, in order to remove all the free acid. White crystalline powder, very sparingly soluble in water. (Herzog.)

				Herzog.
PbO .....	111.8	...	44.57	44.24
18C .....	108	...	43.06	43.34
7H .....	7	...	2.79	2.94
3O .....	24	...	9.88	9.48
<hr/>				
$C^{12}H^7PbO^4$ ....	250.8	...	100.00	100.00

*Ferrous Cinnamate* is pale yellow. (Herzog.)

*Ferric Cinnamate*. — Cinnamate of ammonia forms with sesquichloride of iron an orange-coloured precipitate, not cream-coloured like that produced by benzoate of ammonia. Precipitated by alkaline cinnamates from solution of sesquioxide of iron it is a yellow powder like chrome-yellow. Difficultly soluble in water. (Herzog.)

*Cinnamate of Cobalt*, obtained by precipitating a cobalt solution with an alkaline cinnamate is rose-red. *Cinnamate of Nickel* is greenish white, easily soluble in alcohol. (Herzog.)

*Cinnamate of Copper*. — Alkaline cinnamates precipitate cupric salts of a blue colour like that of the cornflower. (Herzog.) — Warm solutions of cinnamate of ammonia (cinnamate of potash) (Hempel); and of sulphate of copper are mixed, and the salt which immediately precipitates is washed and dried, first in the air then at 100°. (E. Kopp.)

Bluish white, non-crystalline powder, still containing a tolerable quantity of water, the last portions of which cannot be removed without incipient decomposition. (E. Kopp.)

By dry distillation it becomes brown, shrinks together as the decomposition proceeds, and gives off (at 150°, according to Hempel) carbonic acid, which at first contains one-third of carbonic oxide, and afterwards a little carburetted hydrogen gas, while cinnamene (p. 1) passes over as a clear oil, and (from 180°, according to Hempel) cinnamic acid sublimes. (E. Kopp.)

Cinnamate of copper is sparingly soluble in cold water; boiling water decomposes it into an acid and a basic salt. (Herzog.)

*Mercurous Cinnamate* is white and sparingly soluble; *mercuric cinnamate* is white. (Herzog.)

*Cinnamate of Silver*. — *a. Acid?* — Contains 29·3 per cent. of silver. (Marchand.)

*b. Neutral*. — Cinnamate of ammonia is precipitated by a concentrated solution of nitrate of silver, and the salt, which separates in white laminæ (flaky, according to Mulder, and if the cinnamate of ammonia be added to the silver solution, white and curdy, according to Herzog), is pressed between bibulous paper, moistened with water, and again pressed. (Dumas & Peligot.)

It is slowly coloured violet by exposure to light. Somewhat soluble in water (Mulder); insoluble in pure water, but soluble in presence of small quantities of other salts. (Herzog.)

<i>Dried in vacuo at 120°.</i>				Dumas & Peligot.	Mulder.
18 C	.....	108	....	42·33	..... 42·24 .... 41·62
7 H	.....	7	....	2·74	..... 2·92 .... 3·04
Ag	.....	108·1	....	42·38	..... 41·61 .... 42·45
4 O	.....	32	....	12·55	..... 13·23 .... 12·89
$C^{18}H^7AgO^4$ .....				255·1 .... 100·00	..... 100·00 .... 100·00

<i>At 120°.</i>		Fremy.	Herzog.
18 C	.....	41·82	..... 41·77
7 H	.....	2·93	..... 2·89
Ag	.....	42·52	..... 42·31
4 O	.....	12·73	..... 13·03
$C^{18}H^7AgO^4$ .....		100·00	..... 100·00

Bertagnini found 42·69 p. c. silver. The salt contains 43·68 p. c. silver and 1 atom water of crystallization, which is not given off at 100°. (Marchand.)



The alkaline cinnamates form with solutions of *gold* and of *platinum*, yellowish precipitates which blacken in the light. (Herzog.)

Cinnamic acid does not combine with urea. (Hlasiwetz, *J. pr. Chem.* 69, 103.)

Cinnamic acid dissolves easily in *alcohol*, and is precipitated therefrom by water. (Dumas & Peligot.) It dissolves in 4.3 parts of absolute alcohol at  $20^\circ$ . (Mitscherlich.) Dissolves very easily in ether. (Herzog.)

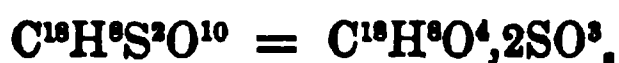
### Thiocinnol.



CAHOURS. *Compt. rend.* 25, 458.

1. When sulphuretted hydrogen is passed to saturation through the alcoholic solution of cinnhydramide, the liquid soon becomes turbid without depositing sulphur, and on standing deposits thiocinnol as a white powder, which is washed with alcohol. — 2. Thiocinnol is also formed when alcoholic oil of cinnamon is treated with sulphide of ammonium.

### Sulphocinnamic Acid.



MARCHAND. *J. pr. Chem.* 16, 60.

HERZOG. *N. Br. Arch.* 20, 164; *J. pr. Chem.* 29, 51.

MITSCHERLICH. *J. pr. Chem.* 22, 197.

#### *Zimmtschwefelsäure.*

First observed (1839) by Marchand, more completely investigated by Herzog in 1848.

*Formation.* By combining cinnamic acid with anhydrous sulphuric acid (Marchand); with common or with fuming oil of vitriol. (Herzog.)

*Preparation.* One part of cinnamic acid is dissolved in from 8 to 12 parts of fuming sulphuric acid of from sp. gr. 1.92 to 1.87, which causes a slight rise of temperature, but no evolution of sulphurous acid; and the mixture is dissolved in water and digested with carbonate of baryta till a filtered sample is no longer precipitated by chloride of barium. The mixture is then filtered, and sulphuric acid is carefully added as long as any precipitate is formed;—or, since it is difficult to hit the right quantity of sulphuric acid, basic acetate of lead is added; the resulting precipitate decomposed by sulphuretted hydrogen; and the filtrate evaporated, first in the water-bath, then in vacuo over oil of vitriol, an amorphous pale yellow residue then remaining, which undergoes no further change at  $100^\circ$ . (Herzog.)

*Properties.* Crystallises from an alcoholic solution in long prisms belonging to the oblique prismatic system, with about 6 atoms of water.

In the air they attract moisture without deliquescing, but in vacuo or at 25° in the air, they give off water, and turn white. The aqueous solution reddens litmus, and has an acid taste. (Herzog.)

<i>Dried at 100°.</i>				Herzog. <i>Mean.</i>
18 C .....	108	...	47.36	47.58
8 H .....	8	...	3.51	3.76
4 O .....	32	...	14.03	13.99
2 SO <sup>3</sup> .....	80	...	35.10	34.67
<hr/>				
C <sup>18</sup> H <sup>8</sup> O <sup>4</sup> , 2SO <sup>3</sup> .....	228	...	100.00	100.00

*Decompositions.* 1. The acid dried at 100° melts when heated, gives off water, and carbonizes without volatilising, giving off aromatic odorous vapours, and leaving a difficultly combustible charcoal. — 2. It dissolves in concentrated nitric acid without disengagement of gas or rise of temperature. On heating the mixture to 44°, a few gas bubbles escape, and at 50° dense red vapours, while crystals form as the liquid cools, and reappear without increasing in quantity when it is heated. No smell of bitter almonds is perceptible, even at 90°. The nitric acid solution mixed with chloride of barium does not form a precipitate of sulphate of baryta, but yields after some time a light crystalline deposit, which, however, does not appear to be sulphocinnamate of baryta. — 3. When sulphocinnamic acid is distilled with alcohol and hydrochloric acid, and the liquid cohobated three times, no foreign substance passes over, but the residue yields on evaporation stellate groups of small crystals, soluble in water and alcohol, which appear to be either sulphocinnamic acid, or sulphocinnamic ether. (Herzog.)

*Combinations. a. With Water.* Sulphocinnamic acid attracts but little moisture in the air, and dissolves readily in water.

*b. With Bases.* Sulphocinnamic acid is bibasic. The neutral salts contain two atoms of base to one atom of acid; in the acid salts, one atom of acid is combined with one atom of base and one atom of water, which cannot be expelled at 100°. The alkaline sulphocinnamates, when heated, leave a residue of alkaline sulphate and sulphite, and when ignited, a residue which gives off sulphuretted hydrogen with acids. The cinnamates of the heavy metals leave metallic sulphides when ignited. The acid and its soluble salts, precipitate the solutions of basic acetate of lead and of mercurous nitrate, and, after some time, that of chloride of barium. (Herzog.)

*Cinnamate of Potash. — a. Neutral.* — The acid is neutralised with carbonate of potash, or the baryta salt decomposed by sulphate of potash. The solution evaporated in vacuo leaves an amorphous yellow mass, which becomes moist in the air, without deliquescing. Perfectly neutral. Gives off 2.91 p. c. water when dried in vacuo at 100°. Dissolves easily in water; with great difficulty in alcohol. (Herzog.)

<i>In vacuo.</i>				Herzog.
2 KO .....	94.4	...	30.12	30.08
C <sup>18</sup> H <sup>6</sup> O <sup>2</sup> , 2SO <sup>3</sup> .....	210	...	67.01	67.01
Aq .....	9	...	2.87	2.91
<hr/>				
C <sup>18</sup> H <sup>6</sup> K <sup>2</sup> O <sup>4</sup> , 2SO <sup>3</sup> + Aq .....	313.4	...	100.00	100.00

*b. Acid.* Crystallises in slender needles from the solution of the neutral salt on the addition of hydrochloric acid. Dissolves with great difficulty in alcohol. (Herzog.)

*Sulphocinnamate of Baryta. — a. Neutral.* — The solution of the baryta-salt obtained in the preparation of sulphocinnamic acid, becomes covered, when evaporated at a gentle heat, with crusts which fall to the bottom, and are renewed until almost all the baryta-salt is separated.

The crusts appear but slightly crystalline, even under the microscope. Permanent in the air. Dried at  $100^\circ$  it gives off 4.87 p. c. = 2 At. water. Nearly insoluble in water (? Gm.) (Herzog.)

<i>Crusts.</i>				Herzog.
2 BaO .....	153.2	...	40.19	..... 40.05
$C^{18}H^6O^3, 2SO^3$ .....	210	...	55.09	
2 Aq .....	18	...	4.72	..... 4.87
<hr/>				
$C^{18}H^6Ba^2O^4, 2SO^3 + 2Aq$ ....	381.2	...	100.00	
<hr/>				
<i>At <math>100^\circ</math>.</i>				
2 BaO .....	153.2	...	42.18	..... 41.92
18 C .....	108	...	29.73	..... 30.08
6 H .....	6	...	1.65	..... 1.79
2 O .....	16	...	4.40	..... 4.44
2 $SO^3$ .....	80	...	22.04	..... 21.77
<hr/>				
$C^{18}H^6Ba^2O^4, 2SO^3$ .....	363.2	...	100.00	..... 100.00

*b. Acid.* — When nitric acid is added to the solution of the baryta-salt obtained in the preparation of sulphocinnamic acid, and evaporated, or when the neutral salt *a* is boiled with water containing nitric acid, the liquid, after some evaporation, deposits on cooling beautiful, delicate needles of the acid-salt. Permanent in the air. Loses its lustre at  $100^\circ$ , and gives off 5.74 per cent. = 2 atoms of water. Sparingly soluble in water and in alcohol. (Herzog.)

<i>At <math>100^\circ</math>.</i>				Herzog.
BaO .....	76.6	...	25.91	..... 25.88
$C^{18}H^7O^3, 2SO^3$ .....	219	...	74.09	
<hr/>				
$C^{18}H^7BaO^4, 2SO^3$ .....	295.6	...	100.00	

*Sulphocinnamate of Baryta and Ammonia.* — The needles of the baryta-salt (*b*) dissolve in dilute ammonia, and yield a double salt in aggregated prisms, which when exposed to the air absorb water and give off ammonia. (Herzog.)

*Sulphocinnamate of Zinc* is crystallisable. (Marchand.) Small nodules. (Herzog.)

*Sulphocinnamate of Copper.* — The solution is easily decomposable, and can only be concentrated under the air-pump. (Herzog.)

*Sulphocinnamate of Silver.* — When neutral sulphocinnamate of baryta is precipitated with nitrate of silver, filtered, and the filtrate evaporated

in the water-bath and then in vacuo, the solution dries up to a grey, lustrous, brittle crust. On evaporating the solution over the open fire reduction is apt to take place, and then, even if a tolerable quantity of liquid is left, the whole suddenly solidifies to a jelly.

The salt when heated yields metallic silver and sulphide of silver. It dissolves easily in hot water, also in nitric acid and in ammonia. (Herzog.)

				Herzog.
2 AgO .....	232.2	....	52.51	..... 52.12
$C^{18}H^{10}O^4, 2SO^3$ .....	210	....	47.49	
<hr/>				
$C^{18}H^6Ag^2O^4, 2SO^3$ .....	442.2	....	100.00	

Sulphocinnamic acid dissolves readily in *alcohol*, and crystallises on spontaneous evaporation.

### Cinnamate of Methyl.



E. KOPP. *Compt. rend.* 21, 1377.

*Zimmtformester, Zimmtkölznaphtha, Cinnamate de methyle.*

Hydrochloric acid gas is passed through a solution of 3 parts of cinnamic acid in 5 parts of absolute alcohol, and the product distilled over oxide of lead.

Colourless oil of sp. gr. 1.106. Boils at 241°. Has a pleasant aromatic odour.

### Cinnamate of Ethyl.



HERZOG. *N. Br. Arch.* 17, 72; 20, 170.

MARCHAND. *J. pr. Chem.* 16, 429; 37, 281.

E. KOPP. *Compt. rend.* 21, 1376; *J. pr. Chem.* 27, 280; *Compt. rend.* 24, 615; *N. J. Pharm.* 11, 72.

*Zimmtvinester, Zimmtnaphtha, Cinnamyläther, Cinnamic ether.*

*Formation.* By passing hydrochloric acid gas into a mixture of cinnamic acid and alcohol. (Herzog, Marchand, Kopp.)

The oil which Plantamour prepared by decomposing cinnamoin with alcoholic potash, is not cinnamic ether. E. Kopp. (It is benzylic alcohol. Kr.)

*Preparation.* 1. A mixture of 1 part of cinnamic acid with 6 parts of alcohol and 2 parts of hydrochloric acid, is distilled down to a third. The residue forms two layers, the lower of which is the ether. It is washed with water; dissolved in water containing alcohol; agitated with a solu-

tion of neutral tartrate of potash, which takes up free acid; decanted from the resulting bitartrate; then filtered, mixed with more water, by which the ether is again precipitated, while tartrate of potash remains in solution; and distilled. The distillate is shaken up with chloride of calcium, and after two days, decanted and rectified. (Herzog.) — 2. Marchand distils 4 parts of absolute alcohol with 2 parts of cinnamic acid and 1 part of hydrochloric acid; pours back several times that which first distils over; then distils till three-fourths have passed over; washes the ether remaining in the retort repeatedly with water; then decants and rectifies over oxide of lead. — 3. The solution of 3 parts of cinnamic acid in 5 parts of alcohol is saturated with hydrochloric acid gas, and the oily product rectified over oxide of lead. (E. Kopp.)

*Properties.* Transparent, rather mobile liquid. More highly refractive than creosote, beautifully iridescent in the light. (Herzog.) Sp. gr. 1.131 (Herzog) at  $12^\circ$  (Marchand); 1.126 at  $0^\circ$  (E. Kopp); 1.0498 at  $20.2^\circ = 1.0656$  at  $0^\circ$ . (H. Kopp.) Boiling point  $262.5^\circ$  (Herzog);  $263^\circ$  at 758 m.m. pressure (Marchand);  $262^\circ$  (E. Kopp);  $260^\circ$  (Hofmann & Blyth);  $261.6^\circ$ , — or, with the correction necessary for the lower temperature of the column of mercury projecting out of the retort,  $266^\circ$ . (H. Kopp. *Ann. Pharm.* 95, 319.) Vapour-density 6.537 at  $291^\circ$ . (Marchand.) Permanent in the air. (Herzog.) Has an agreeably sweet odour of oranges and cinnamon. (Herzog.)

					Herzog.	Marchand.		
					mean.	mean,		
22 C	... ..	132	...	75.00	... ..	74.44	... ..	74.27
12 H	... ..	12	...	6.81	... ..	6.87	... ..	6.81
4 O	... ..	32	...	18.19	... ..	18.69	... ..	18.92
<hr/>								
C <sup>12</sup> H <sup>12</sup> O <sup>4</sup>	... ..	176	...	100.00	... ..	100.00	... ..	100.00

Measures.			
C-vapour	22	9.1520	
H-gas	12	0.8316	
O-gas	2	2.2186	
	2	12.2022	
Ether-vapour	1	6.1011	

*Decompositions.* 1. Cinnamic ether is but little, if at all, decomposed by fuming *nitric acid*. (Marchand.) Concentrated nitric acid converts it, with difficulty, into nitro-cinnamic ether, a considerable quantity of the ether being at the same time decomposed and acid liberated. (E. Kopp.)

2. With alcoholic *ammonia* it forms a crystalline powder (probably cinnamide) but very little in proportion to the ether consumed; the product is not large, even when ammoniacal gas is passed into the ether. (Herzog.)

3. With *potash* it forms cinnamate of potash and alcohol. (Marchand.)

Cinnamic ether is nearly insoluble in *water*, readily soluble in *alcohol* and in *ether*.

## Cinnamein.'



PLANTAMOUR. (1838.) *Ann. Pharm.* 27, 329; 30, 241.

FREMY. *Ann. Chim. Phys.* 70, 189; *Ann. Pharm.* 30, 328.

DEVILLE. *Ann. Pharm.* 74, 280; *J. pr. Chem.* 50, 442; *Ann. Pharm.* 97, 168.

E. KOPP. *Compt. chim.* 1850, 140.

*Oil of Perubalsam.* In the crystallised state, it is the *metacinnamein* of Scharling, not that of Fremy.

*Sources.* In balsam of Peru; according to Simon (*N. Br. Arch.* 29, 181,) ready formed. In tolubalsam (Fremy, Deville), a statement which Scharling disputes. By distilling tolubalsam with water, and repeatedly cohobating the distillate, Deville obtained a small quantity (a gramme from a pound) of volatile oil, from which on rectification *tolene* passed over, while crystallised benzoic acid and cinnamein remained, the latter distilling at 340—350 with partial decomposition. (That which passed over contained 79.86 — 81.12 p. c. C., and 7.62 to 8.83 p. c. H.)

*Formation.* By dissolving cinnamic acid in peruvine, an acid viscous liquid is formed, which, when saturated with hydrochloric acid, yields to boiling water a neutral oil resembling cinnamein and heavier than water. (Scharling.)

*Preparation.* Balsam of Peru is saponified by agitation with excess of caustic potash, and the solid soap dissolved in water: the solution on being warmed separates after a few minutes into two layers, and the upper, which is oily, is to be repeatedly washed with water, till the oil exhibits a faint reddish yellow colour. The residual water is evaporated in the water-bath; the oil dissolved in warm alcohol and evaporated; and this treatment is repeated as long as resin separates out on evaporation. (Plantamour.) — 2. Balsam of Peru dissolved in alcohol of 36° is treated with alcoholic potash, whereby a compound of resin with potash is precipitated; the solution is mixed with water; the cinnamein which separates out in the form of oil is separated from the inferior solution of cinnamate of potash, and dissolved in freshly rectified rock-oil, whereby resin is removed; the rock-oil is then evaporated, and the residual oil placed in a vacuo. Cinnamein thus prepared still retains styracin in solution, the quantity varying according to the nature of the balsam. To free it from this impurity, it is dissolved in weak alcohol, and cooled for several days below 0°, as long as a crystalline deposit of styracin continues to form. (Fremy.) — 3. Balsam of Peru is repeatedly boiled with aqueous carbonate of soda, and the cinnamate of soda is removed by washing, the residue then separating into resin and a yellowish brown liquid which must be heated to 170° on the oil-bath, and distilled in steam heated to 170°. Colourless somewhat milky cinnamein then passes over, and is freed from adhering water by standing for some time in a warm place, over chloride of calcium. Sometimes, perhaps always, the cinnamein thus prepared contains in solution styracin, which partially crystallises out after long standing. (Scharling.) Calcined magnesia or oxide of

lead also separates cinnamein from balsam of Peru, by combining with the cinnamic acid and separating resin. (Simon.)

**Properties.** Faintly coloured (Fremy), colourless, strongly refracting oil (Scharling), which remains liquid when cooled in a freezing mixture for several days (Fremy), to  $-12^\circ$  (Plantamour), to  $15^\circ$  (Scharling) ( $-15^\circ$ ?). When cinnamein is kept under water, there are formed after some time solid crystals (= metacinnamein), which melt at  $12-15^\circ$ , sometimes resolidify after cooling and standing, but after solution in boiling alcohol cannot again be obtained in the crystalline form. (Scharling.) Boils at  $305^\circ$  and distils without decomposition (Plantamour); between  $340$  and  $350^\circ$ , with partial decomposition. (Deville, Fremy.) It has a feeble pleasant odour. Its taste is sharp (Fremy), aromatic, recalling that of fat. (Scharling.) Makes grease spots on paper. (Fremy.) Sp. gr.  $1.098$  at  $14^\circ$ ;  $1.0925$  at  $25^\circ$ . (Scharling.) Neutral.

					Fremy.		Plantamour.
32 C	.....	192	...	80.67	.....	77.68 to 79.08	... 79.55
14 H	.....	14	...	5.88	.....	6.10 „ 6.50	... 6.25
4 O	.....	32	...	13.45	.....	16.27 „ 14.42	... 14.20
<hr/>							
$C^{15}H^8O^4$	.....	238	...	100.00	.....	100.00 100.00	... 100.00

				Scharling.
				Oil. Crystals.
32 C	.....	79.18 to 80.24	...	80.21
14 H	.....	6.56 „ 6.03	...	6.07
4 O	.....	14.26 „ 13.73	...	13.72
<hr/>				
$C^{15}H^8O^4$	.....	100.00	100.00	... 100.00

It is  $C^{15}H^8O^4$ , (Plantamour),  $C^{14}H^8O^3$ . (Fremy.) E. Kopp regarded it as identical with styracin, which Scharling disproved.

**Decompositions.** Cinnamein slowly absorbs moist oxygen. (Fremy.) When exposed for years to air and to light, it assumes a rancid odour and acid reaction. Cinnamein which had been kept for years in a closed vessel had become turbid; when distilled, it began to boil at  $230^\circ$ , and yielded a few drops of a slightly empyreumatic distillate, while a solid substance separated. When the residue was poured into alcohol of  $93^\circ$  Tr., part of it dissolved immediately and the rest on boiling; on cooling, white flakes were deposited which dissolved in boiling alcohol but not in cold alcohol, resembled coagulated albumen when dry, and became transparent at  $120^\circ$  without melting or becoming brittle. These flakes contain  $80.06$  p. c. C. and  $6.23$  p. c. H., and are therefore amorphous cinnamein. — Crystallised cinnamein preserved in a glass vessel for a year, melted to a viscous mass, and in another year became a solid transparent amorphous mass. (Scharling.)

2. Cinnamein is partially decomposed by *distillation*, leaving a small quantity of tar, and yielding a distillate differing in composition from the original substance. (Fremy.) (See page 283.)

3. It is immediately resinized by *oil of vitriol*; the resin purified by boiling with water contains  $70.8$  p. c. C. and  $6.5$  p. c. H., and is therefore cinnamein + water ( $C^{14}H^8O^3 + 4 Aq$ , which requires  $72.0$  p. c. C. and  $6.66$  p. c. H. (Fremy.)

4. Forms a crystalline compound with *chlorine*. (Plantamour.) Slowly



absorbs chlorine, more easily when heated, becoming at the same time coloured and thickened, and when distilled ultimately yields chloride of benzoyl together with an oil. (Fremy.)

5. *Nitric acid* acts briskly on cinnamēin when heated, forming a yellow resin and a large quantity of bitter almond oil. *Peroxide of lead* acts in a similar manner. (Fremy.)

6. Cinnamein forms a crystalline compound with *ammonia*. (Plantamour.)

7. Mixed with *bisulphide of carbon* and powdered hydrate of potash, it forms a saline mass containing xanthate of potash. (Scharling.)

8. Rapidly treated with very concentrated *potash-ley*, or melted with hydrate of potash, it gives off hydrogen, and passes into cinnamate (cinnamate and benzoate) of potash. (Fremy.)

Treated with very concentrated potash-ley in the cold, or with alcoholic potash, it is completely resolved in 24 hours, without disengagement of gas or absorption of oxygen into benzylic alcohol, and cinnamate of potash :



By the continued action of the potash, the benzylic alcohol may be converted into toluol.

In contact with very concentrated solution of potash, cinnamein soon changes its appearance, becomes thicker, and then solid : after 24 hours water dissolves the greater part, and separates peruvín (a mixture of benzylic alcohol and toluol : Kr.) as an oil which floats on the surface. (Fremy.)

Cinnamein solidifies with alcoholic potash to a soft, yellow, pleasant smelling soap. When this soap is dissolved in water, oil separates on the surface, which on distillation passes over as a transparent, aromatic odorous, refracting oil, heavier than water and consisting of cinnamate of ethyl (benzylic alcohol : Krant). By continuing the distillation, water being added to the dry residue, a second clear yellow oil is obtained, of less agreeable aromatic odour, and lighter than water; this oil is the peruvín of Fremy. More of this peruvín is obtained, when water is added to the residue, and the supernatant oil is removed and distilled alone. From the residue in the retort, after solution in water, hydrochloric acid precipitates cinnamic acid and carbobenzoic acid. (Plantamour.) (Cinnamic acid and amorphous benzoic acid. Krant.) By continued boiling of cinnamein with potash-ley, Scharling once obtained Fremy's peruvín; but when he distilled cinnamēin prepared from another balsam, with potash-ley or alcoholic potash, a distillate was obtained which had a different odour and greater specific gravity than peruvín, and dissolved with tolerable facility in water. Separated from this solution by common salt, then dried for some days over chloride of calcium, and distilled, this oil gave off traces of alcohol, and then an oil boiling between 150° and 205° (after rectification at 179°) which was benzylic alcohol, and afterwards a neutral distillate, which solidified in the neck of the retort to a crystalline mass, which, when dissolved in alcohol and exposed to the air, became converted in six weeks into benzoic acid.

Cinnamein scarcely dissolves in *water*. It dissolves in *alcohol* and in *ether*.



## Styracin.



BONASTRE. (1827.) *J. Pharm.* 13, 149; 17, 248; *N. Tr.* 24, 2, 236.

LEPAGE. *J. Chim. med.* 18, 726.

FREMY. *Ann. Chim. Phys.* 70, 196; *Ann. Pharm.* 30, 335.

E. SIMON. *Ann. Pharm.* 31, 272; *N. Br. Arch.* 29, 182; *Ann. Pharm.* 71, 357.

FR. TOEL. *Ann. Pharm.* 70, 1.

AD. STRECKER. *Ann. Pharm.* 70, 10; 74, 112.

JUL. WOLFF. *Ann. Pharm.* 75, 397.

E. KOPP. *Compt. chim.* 1850, 140.

GOSMANN. *Ann. Pharm.* 99, 376.

SCHARLING. *Ann. Pharm.* 97, 90 and 174.

*Metacinnamein.* (Fremy.) *Zimmtsaure.* *Zimmtalcohol.*

Discovered by Bonastre in 1827, investigated by Simon and Toel. Stated by E. Kopp to be identical with cinnamein, which was however disproved by Scharling. The correct formula was first given by Fremy and Strecker.

**Sources.** In liquid storax. — In balsam of Peru; it is often contained in the cinnamein prepared from that substance, and separates from the cinnamein which has been dissolved in weak alcohol, either when cooled several degrees below  $0^{\circ}$ , or after standing for some time. (Scharling.)

**Preparation.** When the solution of liquid storax in alcohol is exposed to a temperature of  $15^{\circ}$  —  $18^{\circ}$ , fine needles separate out in about six months. (Bonastre.) — 2. Fresh liquid storax is treated with cold alcohol, which leaves styracin undissolved. (Bonastre.) — 3. Commercial storax is treated with cold ether; the ether poured off after two days; the residue dissolved in boiling alcohol of  $40^{\circ}$ ; the liquid filtered; and the alcoholic solution allowed to evaporate: styracin then crystallises out, and is obtained pure by washing with cold alcohol, drying between paper, and recrystallisation from alcohol. (The alcoholic solution of storax which has not been treated with ether, likewise deposits styracin on evaporation, but in an impure form: Lepage.) — 4. Liquid storax is distilled with half to seven-tenth parts of crystallised carbonate of soda and water, whereupon styrol passes over; and the residual liquid, which contains cinnamate of soda, is poured off from the resinous mass, which is then washed with water, dried, and dissolved in 20 parts of boiling alcohol of sp. gr. 0.825. The liquid is then filtered; two-thirds of the solution distilled off; and the residue cooled, whereupon almost all the styracin is deposited, as a coarse crystalline powder, which is pressed between paper, repeatedly washed with cold alcohol, and again pressed, till it is no longer sticky from adhering resin, but forms a white dry mass. As this mass still contains soda, it is powdered and dissolved in seven parts of ether; the liquid filtered from the soda-compound; and the ether distilled off in the water-bath: pure styracin then remains. (Simon.) — 5. Toel dries the resinous cake which remains after the distillation of liquid storax, with carbonate of soda and water (4)

after it has been freed from the solution of cinnamate of soda; macerates it repeatedly with cold alcohol, which extracts the colouring resin, and leaves most of the styracin but little coloured; and obtains the styracin quite pure by repeated crystallisation from ether-alcohol. Wolff allows the resinous cake to stand for some time in cold alcohol, when it soon becomes crystalline; frees the crystals from resin by dissolving them in boiling alcohol, and precipitating the resin with sugar of lead; and frequently recrystallises, first from ether-alcohol, then from ether.— 6. After distilling liquid storax with water, and repeatedly boiling out the residue with carbonate of soda, the undissolved portion is slowly allowed to cool to  $30^{\circ}$  —  $40^{\circ}$ : the mass then becomes tough and spongy, and a yellow oil collects in its pores. This oil made to run out by kneading and pressing, and then filtered, solidifies after some time into a crystalline mass, which is purified by recrystallisation from alcohol. The residual mass still contains much styracin, and is therefore worked up for styrone. (E. Kopp.)— 7. After distilling liquid storax with water, and repeatedly boiling the residue with carbonate of soda, the residue separates into a solid dark resin and liquid styracin. The latter is poured off, transferred to a flask, which is placed in an oil-bath at the temperature of  $180^{\circ}$ , and distilled by passing steam heated to  $180^{\circ}$  through it; it then passes over as a white milky oil, which, when freed from water, solidifies on standing in open vessels, to a faintly coloured crystalline mass, which may be recrystallised from alcohol. (Scharling.)— 8. Liquid storax is macerated or digested at a temperature not exceeding  $30^{\circ}$  with five to six parts of dilute soda-ley, till the residue becomes colourless; this residue is collected, washed, dried and dissolved in alcohol containing ether; and from the solution, which, if not colourless, is to be rendered so by treatment with animal charcoal, pure styracin crystallises out. (Gössmann.)

*Properties.* Long, colourless, rectangular prisms, grouped in tufts. (Bonastre, Toel.) Star-shaped crystals. (Simon.) Crystallises from alcoholic solution in very fine, concentrically arranged needles. (Simon.) Separates partially as an oil. (Bonastre.) As hard as wax. (Bonastre.) Melts below  $100^{\circ}$  (Bonastre); at  $38^{\circ}$  (Lepage, E. Kopp);  $44^{\circ}$  (Toel, Scharling);  $50^{\circ}$  (Simon); and therefore melts in boiling water to an oil (floating upon water: Lepage), which solidifies to a noncrystalline mass on cooling. (Simon.) After being crystallised, it does not melt in the heat of the sun. (Scharling.) Fused styracin frequently does not resolidify (E. Kopp); solidifies, long after cooling, in concentrically grouped needles, more rapidly when touched by sharp bodies. (Toel.) Specific gravity of the liquid, 1.085 at  $16^{\circ}5$ . (Scharling.) Tasteless. (Lepage, Toel.) Inodorous. (Toel.) Smells of vanilla (Bonastre); very pleasantly aromatic. (Lepage.) Neutral. Permanent in the air. (Wolff.) Not volatile; on being heated above the melting point, it creeps up the sides of the vessel. (Toel.) Distils without decomposition in steam heated to  $180^{\circ}$ . (Scharling.)

					Marchand.		Toel. <i>mean.</i>		Strecker. <i>mean.</i>	
36 C	.....	216	...	81·82	.....	82·71	...	82·47	...	81·42
16 H	.....	16	...	6·06	.....	6·38	...	6·28	...	6·07
4 O	.....	82	...	12·12	.....	10·91	...	11·25	...	12·51
<hr/>										
C <sup>36</sup> H <sup>16</sup> O <sup>4</sup>	.....	264	...	100·00	.....	100·00	...	100·00	...	100·00

				Wolff.	Scharling.			Fremy.		
					a.	b.				
36 C	.....	216	.....	82.57	....	81.91	....	82.48	....	80.78
16 H	.....	16	.....	6.37	....	6.39	....	6.10	....	6.05
4 O	.....	32	.....	11.06	....	11.70	....	11.42	....	13.17
<hr/>										
C <sup>36</sup> H <sup>16</sup> O <sup>4</sup>	.....	264	.....	100.00	....	100.00	....	100.00	....	100.00

Henry found 76.27 p. c. C, 5.50 H, and 18.23 O. (*J. Pharm.* 20.63.) Toel calculated from his analyses the formula  $C^{60}H^{28}O^8$ ; Strecker, the formula here given. Fremy and Scharling (*b*) examined styracin from Peru balsam.

Polymeric with cinnamic aldehyde.

**Decompositions.** Styracin when not perfectly pure becomes brown in the air. (Wolff.) — 2. It is changed by *nitric acid* to a yellow, pulverisable, tasteless substance, giving off at the same time the odour of bitter almonds. (Lepage.) On distillation with nitric acid, it yields oil of bitter almonds. The rectified distillate contains hydrocyanic acid; the residue in the retort benzoic acid, picric acid, and resin (Simon), benzoic acid and nitrobenzoic acid. (E. Kopp.) — 3. Yields oil of bitter almonds when distilled with *bichromate of potash* (Simon), or with *binoride of manganese* and sulphuric acid (Toel); with chromic acid it gives oil of bitter almonds, benzoic acid and resin. (E. Kopp.) — 4. It is carbonised by cold, more strongly by hot *oil of vitriol* (Lepage), yielding cinnamic acid, and a brown substance insoluble in water and in saline solutions. (E. Kopp.) — 5. Dry *chlorine* changes styracin, with feeble disengagement of heat, into a tough, viscons mass, and at 100° completely, into chlorostyracin. (Toel, E. Kopp.) With chlorine it forms a product resembling chloride of cinnamyl. (Fremy.) — 6. Heated with hydrate of potash, it is completely changed into cinnamate of potash, heat being disengaged. (Fremy.) — 7. If to styracin dissolved in alcohol, a great excess of soda is added, the mass coagulates from separation of the cinnamate of soda, while styrone remains in solution. (Simon.) Distilled with soda-ley, it decomposes into cinnamate of soda and a volatile oil, which distils over (Simon); into cinnamate of soda and styrone. (Toel, Wolff.) — 8. Distilled with hydrate of lime it yields an oil isomeric with benzol, but differing from it and from cinnamene.

**Combinations.** Styracin is completely insoluble in water. It does not combine with lime, even at the boiling heat. (Bonastre.) Neither does it dissolve in ammonia, soda or potash. (Lepage.) It does not combine with acids, but is rendered more soluble by them. The solution of one part of styracin in eight parts of boiling alcohol, which becomes turbid on cooling, is immediately rendered clear by the addition of sulphuric acid, glacial acetic acid, or cinnamic acid. When styracin is dissolved in alcohol containing sulphuric acid, and the solution evaporated in the air, the residue, even after repeated washing with water, contains sulphuric acid, which cannot be extracted by water, but may be recognised by ignition with soda. (Simon.)

Styracin dissolves but sparingly in *alcohol* of 33°, pretty easily in alcohol of 40°. (Lepage.) It dissolves in 21 parts of cold, in 3 parts of boiling alcohol of sp. gr. 0.825 (Simon); the solution is rendered milky by water. (Lepage.) It is but sparingly soluble in cold alcohol of 93° Tr., the hot saturated solution deposits oil or crystals on cooling. (Scharling.)

It dissolves in 3 parts of cold *ether*, but crystallises less beautifully from this solution than from alcohol. (Simon.) The solution of styracin in ether-alcohol forms, before the commencement of the crystallisation, two layers, the upper of which is principally ether containing a little particularly pure styracin, while the lower yellowish layer contains alcohol and almost all the styracin. This layer becomes gradually turbid, and solidifies to verrucose crystals when touched with sharp substances. (Wolff.)

### Appendix.

*Cinnamate of styracin, Acid cinnamate of styracin, Acid cinnamate of styrone.*

Remains in the water left in the distilling vessel, when liquid storax is distilled with water, and is obtained in beautiful crystals by evaporation and boiling the solution with animal charcoal. (Simon.)

Acids precipitate cinnamic acid from the aqueous solution of cinnamate of styracin; alkalis precipitate styracin. The compound dissolves in 60 to 70 parts of cold alcohol. (Simon.)

### Myroxocarpin.

STENHOUSE. *Ann. Pharm.* 77, 306.

SCHARLING. *Ann. Pharm.* 97, 69.

*Sources.* In the white balsam of *Sonsonate*, and of *San Salvador* (Guatemala) which, according to Pereira, is obtained by pressure from the fruit of a *myrospermum*. (Stenhouse, Scharling.)

*Preparation.* The balsam is digested with alcohol, and the crystals which separate after 12 hours are collected, and purified by repeated recrystallisation with a little animal charcoal. One pound of balsam yields an ounce of myroxocarpin. (Stenhouse.)

*Properties.* Broad thin prisms, more than an inch long, belonging to the right prismatic system, and having the lustre of nitrate of silver.  $\infty P. oP. \infty \check{P} \infty. \check{P} \infty. 2\check{P} \infty. \bar{P} \infty. 2\bar{P} \infty$  ( $\infty P : \infty P = 102^\circ 12'$ ;  $\bar{P} \infty : o\bar{P} = 127^\circ 4'$ ;  $2\bar{P} \infty : oP = 110^\circ 41'$ ;  $\check{P} \infty : oP = 133^\circ 7'$ ;  $2\check{P} \infty : oP = 115^\circ 5'$ . Ratio of the principal axis to the lateral axes = 1 : 0.9363 : 0.7553. (Miller.)

Hard and brittle. Tasteless. Inodorous. Neutral. Does not lose weight at  $100^\circ$ . Melts at  $115^\circ$  to a transparent glass which does not crystallise on cooling, but only after solution in alcohol. (Stenhouse.)

Calculation according to Stenhouse.				Stenhouse.
				<i>mean.</i>
48 C .....	288	....	77.63	..... 77.10
35 H .....	35	....	9.43	..... 9.51
6 O .....	48	....	12.94	..... 13.39
<hr/>				
$C^{48}H^{35}O^6$ .....	371	....	100.00	..... 100.00

**Decompositions.** When heated above the melting point, it sublimes but partially, the residue being changed into resin, with formation of a large quantity of acetic acid. — 2. Suspended in water it is very slowly changed into a chlorinated resin, which, after being washed with water and dissolved in alcohol, imparts to it an acid reaction. — 3. By strong *nitric acid* with the aid of heat, it is slowly changed into oxalic acid, without formation of picric acid or any particular acid. (Stenhouse.)

Does not dissolve in water, either cold or hot.

Does not dissolve in acids or alkalis, and is not changed by boiling potash.

Dissolves partially in cold alcohol, and in ether, readily in the same liquids when warm. (Stenhouse.)

### Resin from Tolu-balsam.

FREMY. *Ann. Chim. Phys.* 70, 199; *Ann. Pharm.* 30, 337.

H. DEVILLE. *N. Ann. Chim. Phys.* 3, 163.

E. KOPP. *Compt. chim.* 1849, 150.

According to Fremy, the resins of Peru-balsam, of Tolu-balsam, and of benzoin are the same, and have the same composition as the resin produced by oil of vitriol from cinnamoin, viz.  $C^{54}H^{30}O^{12} =$  cinnamoin + water. They give a beautiful red coloration with oil of vitriol.

			Fremy.		
	<i>a.</i>		<i>b.</i>		<i>c.</i>
C .....	71.05	.....	69.97	....	70.48
H .....	6.94	.....	6.20	....	6.58
O .....	22.01	.....	23.83	....	22.94
	100.00	.....	100.00	....	100.00

From balsam of Tolu, Kopp obtained  $\alpha$ - and  $\beta$ -resin; Deville only obtained  $\alpha$ -resin agreeing with Kopp's  $\beta$ -resin. (But by his method of preparation,  $\alpha$ -resin might, by absorbing oxygen, pass into  $\beta$ -resin. Fremy's analyses agree with a mixture of  $\alpha$ - and  $\beta$ -resin. Kr.)

**$\alpha$ -resin.** Tolu balsam freed from volatile oil and from cinnamic acid is exhausted with cold alcohol; the solution is evaporated, and the residual brown, brittle resin, to which alcohol tenaciously adheres, is boiled with water containing hydrochloric acid, to extract the carbonate of soda as completely as possible, then powdered and dried in vacuo, first at the ordinary temperature, and afterwards at  $100^\circ$ . It is obtained perfectly pure by drenching it with cold alcohol, pouring off the alcohol after a short time, evaporating the solution, and treating the powdered residue four or five times for five minutes with alcohol or ether. The last solution leaves pure  $\alpha$ -resin on evaporation.

Brown, lustrous resin. Brittle when cold. Cakes together after being powdered even at 16°, and melts completely at 60°.

				E. Kopp.	
36 C .....	216	...	72.48	.....	72.19
18 H .....	18	...	6.04	.....	6.38
8 O .....	64	...	21.58	.....	21.43
<hr/>					
C <sup>36</sup> H <sup>18</sup> O <sup>8</sup> .....	298	...	100.00	.....	100.00

The resin contained 0.5 per cent. of carbonate of lime and carbonate of soda, which were allowed for in the calculation.

*Decompositions.* When exposed in the state of powder to moist air and to light, it becomes darker and heavier; afterwards gives up but little cinnamic acid to dilute aqueous carbonate of soda; and is no longer completely soluble in cold alcohol, but leaves a residue of  $\beta$ -resin. Dissolved in potash it absorbs oxygen; acids then precipitate  $\beta$ -resin.

2. Burns with a bright fuliginous flame.

3. By dry distillation it yields gases consisting of carbonic oxide and carbonic acid, an oil which is changed by caustic potash into toluol and benzoic acid, and another clear neutral oil, which boils above 250°, and is carbonised by oil of vitriol.

4. It is coloured red by oil of vitriol, and dissolved even in the cold; after a short time, water precipitates a red resin free from sulphuric acid; after a longer action of the oil of vitriol, water produces no precipitate, the red solution then containing a conjugated sulphuric acid.

5. By treating the resin with nitric acid, coloured amorphous benzoic acid (xii, 46) is formed, together with oil of bitter almonds, hydrocyanic acid, a little carbonic acid, and much nitrogen. No picric acid is produced at the same time.

6. On distilling the resin with concentrated potash-ley, toluol and water pass over; from the residue in the retort after solution in water, acids precipitate benzoic acid and resin. (Kopp.)

It colours water yellow after long boiling. Dissolves easily in aqueous caustic alkalis; by concentrated potash, a brown resinate of potash is precipitated, which dissolves in pure water.

Dissolves readily in cold alcohol and in ether.

*$\beta$ -resin.* Remains after the balsam has been exhausted with cold alcohol. Powdered balsam of Tolu, freed from volatile oil and cinnamic acid, is treated eight or ten times with renewed quantities of cold alcohol and ether; and the residue is boiled with slightly acid water in order to remove the alcohol. (Kopp.) Balsam of Tolu is boiled with as little potash-ley as possible, and the liquid is greatly diluted and saturated with carbonic acid, by which the resinate of potash is partially decomposed and resin is precipitated. Chloride of calcium is then added; the precipitate of carbonate and resinate of lime collected on a filter, and decomposed by hydrochloric acid; the residue dissolved in alcohol; and the solution precipitated by water. (Deville.)

*Properties.* Pale, yellowish brown, brittle, easily pulverisable, inodorous, and tasteless resin, which melts only above 100°. (Kopp.) Rose-red powder, the colour of which appears to be changed by air and light. Smells faintly of vanilla. Readily attracts moisture. When pure, it remains pulverulent at 102° to 103° C. (Deville.)

						Deville.		Kopp.
36 C	.....	216	....	68.35	.....	68.24	....	68.29
20 H	.....	20	....	6.32	.....	6.60	....	6.41
10 O	.....	80	....	25.33	.....	25.16	....	25.30
<hr/>								
$C^{36}H^{20}O^{10}$	.....	316	....	100.00	.....	100.00	....	100.00

After subtracting 2.5 p. c. ash. (E. Kopp.)

*Decompositions.* 1. With fuming *nitric acid*, it takes fire and burns. (Deville.) It is changed by nitric acid like *a-resin*. Nitric acid containing chlorine (but not that which is free from chlorine), converts it into oxalic acid. (Kopp.)—2. When treated with concentrated *potash-ley*, it yields at first, very little volatile oil, which is formed only at a very high temperature and when the mass has become dry, and finally it carbonise (Kopp.)

Dissolves in cold *oil of vitriol* with reddish brown colour; the solution becomes violet by attracting moisture from the air. Dissolves in potash (even very dilute, according to Deville) with dark brown colour. (Kopp.)

Dissolves in alcohol (Deville); is but sparingly soluble in cold alcohol and ether. (Kopp.)

### Cinnamic Anhydride.



GERHARDT. (1852.) *N. Ann. Chim. Phys.* 37, 285; *Ann. Pharm.* 87, 76; *Traité* 3, 387.

*Anhydrous cinnamic acid, Zimmtsäure-Anhydrid, wasserfreie Zimmtsäure. Cinnamate cinnamique ou de cinnamyle.*

Formed by the action of chloride of cinnamyl on oxalate of potash, or of pentachloride of phosphorus on cinnamate of soda.

*Preparation.* Six parts of cinnamate of soda are treated with one part of pentachloride of phosphorus, as in the preparation of anhydrous benzoic acid (xii, 93), and the product is washed with cold water and aqueous carbonate of soda, and crystallised from boiling alcohol.

White crystalline powder, consisting of microscopic needles. Fuses at 127° C.

						Gerhardt.
						mean.
36 C	.....	216	....	77.69	.....	77.43
14 H	.....	14	....	5.03	.....	5.08
6 O	.....	48	....	17.28	....	17.49
<hr/>						
$C^{36}H^{14}O^6$	.....	278	....	100.00	.....	100.00

Becomes acid with boiling water. Does not dissolve in water, and scarcely in cold alcohol, but more easily in boiling alcohol.



### Aceto-cinnamic Anhydride.



GERHARDT. (1852.) *N. Ann. Chim. Phys.* 37, 385.

*Anhydrous aceto-cinnamic acid, Acetate de cinnamyle, Cinnamate d'acetyle.*

Chloride of acetyl acts with considerable disengagement of heat on cinnamate of soda, forming a product which smells strongly of acetic anhydride, and continually gives off carbonic acid when washed with aqueous carbonate of soda. Ether extracts from the residual pasty mass an oil mixed with cinnamic acid, which is exactly like benzo-acetic anhydride.

### Benzo-cinnamic Anhydride.



GERHARDT. (1852.) *N. Ann. Chim. Phys.* 37, 385.

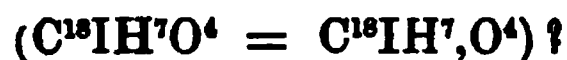
Obtained by the action of 7 parts of chloride of benzoyl on 10 parts of cinnamate of soda.

Fatty oil. Sp. gr. 1.184 at 23°.

In moist air it gradually becomes acid. It is changed by alkalis into alkaline cinnamate and benzoate. By distillation it is decomposed and yields a yellowish oil smelling of cinnamene, which gradually deposits crystals of anhydrous benzoic acid and an acid liquid. Soluble in carbonate of soda.

*Iodine-nucleus*  $C^{18}IH^7$ .

### Iodocinnamic Acid.



HERZOG. *N. Br. Arch.* 20, 167.

When cinnamic acid is melted with excess of iodine, and the dark brown mass is boiled with water till all the free iodine is evaporated, the liquid, on cooling, yields colourless crystals of iodocinnamic acid.

Crystallises from alcohol in small, stellate crystals, which become somewhat yellow in the air. Dissolves easily in hot water and in alcohol.



*Bromine-nucleus*  $C^{18}BrH^7$ .**Bromocinnamic Acid.**HERZOG. *N. Br. Arch.* 20, 166.

Bromine vapour is passed over cinnamate of silver until excess of bromine shows itself in brown yellow vapours in the closed vessel; the decomposed salt is treated with ether; and the solution is filtered and left to evaporate. A thick oil then remains, which is colourless at first, but becomes pale yellow in 24 hours. This oil dissolves partially in potash, a colourless oil of penetrating aniseed odour remaining undissolved (probably a bromide of carbon) which is produced by the action of bromine upon the ether. The alkaline solution, after being saturated with hydrochloric acid, deposits in 48 hours small white crystals of bromocinnamic acid.

Decomposes somewhat on solution in water and evaporation. Forms easily soluble salts with all bases. Does not precipitate nitrate of silver.

*Chlorine-nucleus*  $C^{18}ClH^7$ .**Chloride of Cinnamyl.**FREMY. *Ann. Chim. Phys.* 70, 196; *Ann. Pharm.* 30, 336.CAHOURS. *Compt. rend.* 22, 846; *Ann. Pharm.* 60, 254; *N. Ann.**Chim. Phys.* 23, 341; *J. pr. Chem.* 45, 140; *Ann. Pharm.* 70, 42.BÉCHAMP. *Compt. rend.* 42, 224; *J. pr. Chem.* 68, 489.

*Formation.* 1. By the action of pentachloride of phosphorus on cinnamic acid. (Cahours.) — 2. By the action of terchloride or terbromide of phosphorus on cinnamic acid. (Béchamp.)



3. By treating styracin with chlorine, a body is formed which appears to possess the properties of chloride of cinnamyl.

*Preparation.* 1. When cinnamic acid is treated with pentachloride of phosphorus, hydrochloric acid is given off in abundance, and oxychloride of phosphorus and chloride of cinnamyl pass over. This product is rectified; the fraction between  $250^\circ$  —  $265^\circ$  is collected separately and washed with a small quantity of cold water, which is poured off; and the chloride of cinnamyl is dried over chloride of calcium and rectified. (Cahours.) — 2. Dry cinnamic acid is placed in a flask provided with a drawn out tube, terchloride of phosphorus added, and the whole gradually

heated to between  $60^{\circ}$  —  $120^{\circ}$  as long as hydrochloric acid is disengaged. The mixture melts, and forms two layers, the upper of which consisting of chloride of cinnamyl, is decanted and distilled. (Béchamp.)

Heavy oil of sp. gr. 1.207. Boils at  $262^{\circ}$ .

				Cahours.	
18 C	.....	108	....	64.90	..... 64.60
7 H	.....	7	....	4.20	..... 4.00
Cl	.....	35.6	....	21.28	..... 21.42
2 O	.....	16	....	9.62	..... 9.98
<hr/>					
$C^{18}H^7ClO^2$	.....	166.6	....	100.00	..... 100.00

In moist air it rapidly becomes acid, forming hydrochloric acid and beautifully crystallising cinnamic acid. (Cahours.)

With dry ammoniacal gas it yields sal-ammoniac and a white solid substance, which dissolves in boiling water, and crystallises on cooling in delicate needles like benzamide. (Cahours.)

Distilled with cyanide of potassium or cyanide of mercury, it yields chloride of potassium or of mercury and cyanide of cinnamyl.

With alcohol, it becomes strongly heated and forms cinnamic ether, which is precipitated by water as an oil.

With aniline it forms cinnanilide, with considerable evolution of heat. (Cahours.)

### Chlorocinnamic Acid.



E. KOPP. *Compt. rend.* 24, 614; *N. J. Pharm.* 16, 426; *J. pr. Chem.* 41, 425.

TOEL. *Ann. Pharm.* 70, 7.

*Chlorzimmtsäure, Acide chlorocinnamique.*

**Formation.** By passing chlorine into a cold solution of cinnamic acid in concentrated carbonate of soda. (Kopp.) By the action of potash on chlorostyracin, with simultaneous formation of a chlorinated oil and of chloride of potassium. (Toel.) The product which Herzog obtained (*N. Br. Arch.* 20, 165; 23, 17) by the action of chlorine on dry cinnamic acid, appears to be chlorobenzoic acid. (See page 272.)

**Preparation.** When alcoholic chlorostyracin is mixed with excess of alcoholic potash, the mixture soon solidifies to a magma of chloride of potassium and chlorocinnamate of potash. This is collected on a filter and washed with alcohol, pressed, dissolved in a little boiling alcohol, and mixed with excess of hydrochloric acid: on cooling, chlorocinnamic acid crystallises, and is purified by recrystallisation. (Toel.)

**Properties.** Long, lustrous, flexible needles. Melts at  $132^{\circ}$ ; may be sublimed at a strong heat. Inodorous in the cold. The vapour strongly excites coughing. Reddens litmus.

					Toel.
18 C	.....	108	...	59.23	..... 59.35
Cl	.....	35.6	..	19.41	.... 19.00
7 H	.....	7	...	3.82	..... 4.04
4 O	.....	32	...	17.54	..... 17.61
<hr/>					
$C^{18}ClH^7O^4$	.....	182.6	...	100.00	..... 100.00

Sparingly soluble in cold water (less easily than chlorobenzoic acid, Kopp), more easily in hot water. When it is boiled with a little water, the undissolved portion melts to an oil. (Toel.)

The chlorocinnamates crystallise less readily than the chlorobenzoates. (Kopp.)

*Chlorocinnamate of Ammonia.* — Arboriform curved needles, containing 1 atom of water of crystallisation.

					Toel.
$NH^4O$	.....	26	...	12.41	..... 12.91
$C^{18}ClH^6O^3$	.....	173.6	...	83.22	
Aq	.....	9	...	4.37	
<hr/>					
$C^{18}NH^4ClH^6O^4 + Aq$	....	208.6	..	100.00	

*Chlorocinnamate of Potash* forms lustrous, pearly flakes. (Toel.)

*Chlorocinnamate of Baryta.* — Obtained by precipitating the ammonia-salt with chloride of barium, as a white powder soluble in boiling water, and crystallising out in lustrous laminæ. When ignited, it leaves the baryta as chloride of barium. After being dried over oil of vitriol, it loses 3.80 p. c. in a current of air at  $110^\circ$ , and then nothing more at  $270^\circ$ .

					Toel.
BaO	.....	76.6	...	29.51	..... 29.50
18 C	.....	108	...	41.76	..... 41.29
Cl	.....	35.6	...	13.69	..... 13.63
6 H	.....	6	...	2.31	..... 2.44
3 O	.....	24	...	9.26	..... 9.34
Aq	.....	9	...	3.47	.... 3.80
<hr/>					
$C^{18}BaClH^6O^4 + Aq$	.....	259.2	...	100.00	..... 100.00

*Chlorocinnamate of Lime.* — Resembles the ammonia-salt. Sparingly soluble. (Toel.)

*Chlorocinnamate of Silver.* — Obtained by double decomposition from hot solutions, in the form of slender needles which blacken in the light. Contains no water of crystallisation. (Toel.)

					Toel.
<i>Dried at <math>200^\circ</math>.</i>					
AgO	.....	116.1	...	40.08	..... 40.03
$C^{18}ClH^7O^3$	.....	173.6	...	59.92	
<hr/>					
$C^{18}AgClH^6O^4$	.....	289.7	...	100.00	

Chlorocinnamic acid dissolves easily in *alcohol* and in *ether*. (Toel.) In alcohol less easily than chlorobenzoic acid. (Kopp.)

## Chlorinated Oil from Cinnamic Acid.

HERZOG. *N. Br. Arch.* 20, 165; 23, 17.

J. STENHOUSE. *Phil. Mag. J.* 19, 38; *J. pr. Chem.* 26, 126; *Ann. Pharm.* 55, 3; *Phil. Mag. J.* 7, 27, 130; *Ann. Pharm.* 57, 79; *J. pr. Chem.* 37, 288; *Phil. Mag. J.* 27, 366.

E. KOPP. *Compt. rend.* 24, 614; *N. J. Pharm.* 11, 426; *J. pr. Chem.* 41, 425.

**Formation** By the action of chlorine upon dry cinnamic acid (Herzog), of chlorine (chlorate of potash and hydrochloric acid: Hofmann), or hypochlorite of lime, on a warm aqueous solution of cinnamic acid (Stenhouse); by passing chlorine into a heated solution of cinnamic acid in carbonate of soda (Kopp). In all these cases, chlorobenzoic acid or benzoic acid is simultaneously formed.

**Preparation.** When the mixture of chlorobenzoate of potash and chlorinated oil, — obtained as described at page 272, 6, by treating with carbonate of potash the product of the action of chlorine on cinnamic acid, — is digested with animal charcoal, the charcoal extracts the oil and gives it up again to alcohol. (Herzog.)

2. When cinnamic acid is distilled with a saturated solution of hypochlorite of lime, this oil passes over, together with water and acid; it is washed with water, and then placed in contact with pieces of caustic lime and chloride of calcium, in order to free it from hydrochloric acid and water. The oil which, after being poured off, is strongly alkaline, yields by distillation, first a colourless neutral distillate, and then, with decomposition, an acid and yellowish distillate; the latter distillate emits vapours of hydrochloric acid, and is therefore distilled again with water (resin then remaining), and the distillate, which is now colourless and neutral, is dried in vacuo over oil of vitriol. (Stenhouse.)

**Properties.** Heavier than water. Has a peculiar aromatic smell, at once like oil of bitter almonds and oil of winter-green. Has a sharp, burning taste, like cress. Neutral. (Stenhouse.)

	Stenhouse.		
	<i>a.</i>	<i>b.</i>	<i>c.</i>
C .....	67.33	68.84	70.55
H .....	4.89	5.35	5.46
Cl .....	24.62	24.17	18.36
	96.84	98.36	94.37

*a.* The first neutral portion distilled alone, after standing with lime and chloride of calcium. *b* and *c.* Products of different preparation distilled with water and dried over oil of vitriol.

Appears to be a hydrocarbon in which hydrogen is replaced by chlorine. (Stenhouse.)

**Decompositions.** May be easily set on fire, and burns with a green flame, giving off hydrochloric acid vapours. When heated, it is coloured

red by *oil of vitriol*, and then carbonised. When it is heated with *nitric acid*, binoxide of nitrogen is evolved in abundance, and on cooling, crystallised nitrobenzoic acid is formed. It is not changed either by aqueous *ammonia* or by ammoniacal gas. By boiling with *potash-ley*, it is partially decomposed, with formation of chloride of potassium. With *sodium*, it gives off gas, which is perhaps hydrogen, becomes hot, and at length takes fire with explosion. (Stenhouse.)

Dissolves with difficulty in water, easily in alcohol, and is precipitated by water. (Herzog.)

With this oil is probably identical the oil which Toel obtained by acting with alcoholic potash on an alcoholic solution of chlorostyracin (p, 299), filtering off the liquor from the resulting chloride of potassium and chlorocinnamate of potash, evaporating the alcohol, and precipitating with water. According to Toel, it is a tolerably colourless oil which may be distilled with water without decomposition, has a peculiar odour, and a sharp burning taste. It rapidly becomes brown in the air, burns with green-edged flame when set on fire, and dissolves with tolerable facility in water.

*Chlorine-nucleus*  $C^{18}Cl^4H^4$ .

### Tetrachlorocinnamyl.



DUMAS & PELIGOT. *Ann. Chim. Phys.* 57, 316.

*Tetrachlorocinnamyl, Chlorocinnose, Hydrure de quadrichlorocinnamyle.*

Oil of cinnamon is distilled four or five times in a stream of chlorine, until the distillate in the receiver solidifies in long white needles, which may be obtained pure by pressing between paper.

Beautiful, dazzling white needles. Melts and sublimes unchanged at a gentle heat.

					Dumas & Peligot.
18 C	.....	108	....	39·94	..... 39·33
4 Cl	.....	142·4	....	52·66	..... 52·75
4 H	.....	4	....	1·48	.... 1·85
2 O	.....	16	....	5·92	..... 6 07
<hr/>					
$C^{18}Cl^4H^4O^2$	.....	270·4	....	100·00	..... 100·00

It is not changed by boiling oil of vitriol. Not altered by distillation in dry ammoniacal-gas.

Dissolves in boiling alcohol, and crystallises on cooling.

## Chlorostyracin.



TOEL. *Ann. Pharm.* 70, 6.

STRECKER. *Ann. Pharm.* 70, 10.

E. KOPP. *Compt. chim.* 1850, 144.

Dry chlorine is passed over styracin, ultimately at 100°, and the product is freed from excess of chlorine by repeated solution in alcohol and evaporation.

Yellow, tough, sticky mass. Smells like balsam of copaiva. Has a sharp and grating taste.

					Toel.
36 C	.....	216	....	53.68	..... 53.64
4 Cl	.....	142.4	....	35.38	..... 35.50
12 H	.....	12	....	2.98	
4 O	.....	32	....	7.96	
<hr/>					
$\text{C}^{36}\text{Cl}^4\text{H}^{12}\text{O}^4$	.....	402.4	....	100.00	

Toel at first proposed the formula  $\text{C}^{60}\text{Cl}^7\text{H}^{21}\text{O}^8$ .

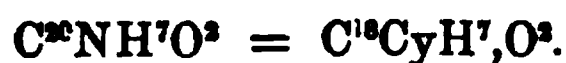
Its alcoholic solution left to stand with excess of alcoholic potash, decomposes into chloride of potassium, chlorocinnamate of potash, and a chlorinated oil, which remains dissolved in alcohol (p. 298). (Toel.)

Distilled in a stream of chlorine, it yields a volatile chlorinated oil, and a crystallisable chlorinated acid which forms salts very readily crystallisable. (E. Kopp.)

Chlorostyracin does not dissolve in water. It dissolves in hot alcohol and ether, from which it again separates as an amorphous mass. (Toel.)

*Cyanogen-nucleus*  $\text{C}^{18}\text{CyH}^7$ .

**Cyanide of Cinnamyl.**



CAHOURS. *N. Ann. Chim. Phys.* 23, 341; *J. pr. Chem.* 45, 140; *Ann. Pharm.* 70, 42.

In the distillation of chloride of cinnamyl with cyanide of potassium or cyanide of mercury, a liquid passes over which rapidly becomes brown in the air, while hydrocyanic acid and cinnamic acid are formed. This liquid still contains chlorine, but is composed for the most part of cyanide of cinnamyl.

					Cabours.
20 C	.....	120	....	76.35	..... 72.23
N	.....	14	....	9.01	..... 7.44
7 H	.....	7	....	4.45	..... 4.39
2 O	.....	16	....	10.19	..... 15.94
<hr/>					
$C^{20}NH^7O^2$	.....	157	....	100.00	..... 100.00

*Nitro-nucleus*  $C^{18}XH^7$ .

### Nitrocinnamic Acid.



MITSCHERLICH. (1841.) *N. Ann. Chim. Phys.* 4, 73; 7, 5; *J. pr. Chem.* 22, 192.

E. KOPP. *Compt. rend.* 24, 614; *N. J. Pharm.* 11, 426; *J. pr. Chem.* 41, 425; *Compt. chim.* 1849, 146.

J. WOLFF. *Ann. Pharm.* 75, 303.

*Nitrozimmtsäure, Zimmtsälpetersäure.*

*Formation.* 1. By the action of concentrated nitric acid on cinnamic acid. (Mitscherlich, Kopp.)—2. By heating styrene with nitric acid, with addition of urea (p. 257). (Wolff.)

*Preparation.* Concentrated nitric acid is freed from nitrous acid by boiling, and after cooling, about one-eighth of cinnamic acid is added. The cinnamic acid dissolves in a few minutes, without disengagement of gas, the liquid becomes heated to  $40^\circ$ , and a mass of crystals is deposited. In order to obtain larger quantities, cinnamic acid is triturated with nitric acid, and cooled, so that the temperature may not rise above  $50^\circ$ ; the mass is washed with cold water, till all nitric acid is removed, then dissolved in boiling alcohol, and filtered; and the resulting crystals are washed with cold alcohol. (Mitscherlich.) Kopp dissolves 1 part of powdered cinnamic acid in 3 parts of monohydrated nitric acid, freed from nitrous acid by passing a dry stream of air through it, the mixture then solidifying almost immediately in consequence of the crystallisation of the nitrocinnamic acid; washes the magma with water; then dries and sets it aside for 24 hours with 4 parts of cold alcohol, which removes any benzoic acid that may be present.

*Properties.* Very small, white crystals, with a faint yellowish tint. Melts at about  $270^\circ$ , and solidifies to a mass of crystals on cooling. Boils a little above  $270^\circ$  with decomposition. (Mitscherlich.)

					Mitscherlich.	Wolff.
18 C	.....	108	....	55.95	..... 55.57	.... 55.6
N	.....	14	....	7.25	..... 7.73	
7 H	.....	7	....	3.62	..... 3.64	.... 4.0
8 O	.....	64	....	33.18	..... 33.06	
<hr/>						
$C^{18}XH^7O^4$	.....	193	....	100.00	..... 100.00	

Forms carbostyryl with *sulphide of ammonium*. (Chiozza.) When nitrocinnamic acid is dissolved in alcoholic sulphide of ammonium, sulphur separates on gently warming the liquid, while a yellow resin and an alkaloid remain dissolved. The latter is colourless and crystallisable, does not dissolve in water, but is soluble in alcohol and in ether, and forms difficultly crystallisable salts. (E. Kopp.)

Nitrocinnamic acid may be boiled with excess of alkali without decomposition.

Nitrocinnamic acid scarcely dissolves in cold water, and very little in boiling water. It does not melt to an oil when boiled with water.

It is slightly soluble without decomposition in boiling hydrochloric acid. With bases, it acts as a feeble acid and expels carbonic acid. The salts with alkaline bases are obtained by dissolving the acid in the aqueous base; the rest are obtained by precipitating with the ammonia-salt. The nitrocinnamates of ammonia, potash, and soda, are readily soluble; the others are sparingly soluble, or insoluble. Strong acids decompose them, liberating nitrocinnamic acid.

*Nitrocinnamate of Ammonia*. — The solution gives off ammonia when evaporated, and deposits nitrocinnamic acid in indistinct crystals.

*Nitrocinnamate of Potash*. — Deposited in nodules when the solution is evaporated; on addition of caustic potash, it is deposited in distinct prisms. Permanent in the air.

*Nitrocinnamate of Magnesia*. — With magnesia-salts, nitrocinnamate of ammonia forms, after some time, nodular crystalline groups which dissolves with tolerable facility in water.

*Nitrocinnamate of Silver* is precipitated in the pulverulent form on adding the ammonia-salt to nitrate of silver. After being dried at  $100^{\circ}$ , it does not give off water at  $140^{\circ}$ , at which point decomposition begins. When carefully heated, it decomposes so gradually that no silver escapes as dust. Very sparingly soluble in water.

<i>Dried at <math>100^{\circ}</math>.</i>				<i>Mitscherlich.</i>	
AgO .....	116	...	38.66	.....	38.18
C <sup>18</sup> XH <sup>6</sup> O <sup>3</sup> .....	184	...	61.84		
<hr/>					
C <sup>18</sup> AgXH <sup>6</sup> O <sup>4</sup> ....	300	...	100.00		

Nitrocinnamic acid dissolves in 327 parts of absolute *alcohol* at  $20^{\circ}$ . (Mitscherlich.)

### Nitrocinnamate of Ethyl.



MITSCHERLICH. (1841.) *J. pr. Chem.* 22, 194.

E. KOPP, *Compt. rend.* 24, 615; *N. J. Pharm.* 11, 72.

*Nitrocinnamic ether, Nitrozimmtvinester, Zimmtsälpetersäure-naptha.*

*Formation.* By heating together nitrocinnamic acid with alcohol and



### 302 PRIMARY NUCLEUS $C^{18}H^8$ : OXYAMIDOGEN-NUCLEUS $C^{18}AdH^8O^2$ .

oil of vitriol. (Mitscherlich.) By the action of concentrated nitric acid on cinnamic ether. (E. Kopp.)

*Preparation.* When 1 part of nitrocinnamic acid is heated with 20 parts of absolute alcohol and a little oil of vitriol, at a temperature not exceeding  $80^\circ$ , the acid gradually dissolves, and the ether crystallises out on cooling. It is dissolved in alcohol containing ammonia, and allowed to crystallise.

Prisms which melt at  $136^\circ$ . Boils at about  $300^\circ$  with decomposition.

				Mitscherlich.
22 C .....	132	...	59.73	..... 58.88
N .....	14	...	6.34	
11 H .....	11	...	4.97	..... 4.96
8 O .....	64	...	28.96	
<hr/>				
$C^{22}NH^{11}O^8$ .....	221	...	100.00	

By boiling with potash it is converted into nitrocinnamate of potash and alcohol.

### Nitrocinnamic Anhydride.



CHIOZZA. (1853.) *N. Ann. Chim. Phys.* 39, 231; *Compt. rend.* 36, 631; *Gerhardt, Traité* 3, 388.

Formed by the action of oxychloride of phosphorus on nitrocinnamate of potash.

Melts in boiling water more easily than nitrocinnamic acid, forming a yellow resin which is easily kneaded.

Readily takes up water, and is converted into nitrocinnamic acid. With ammonia it easily forms nitrocinnamide and nitrocinnamate of ammonia. With alcohol it forms nitrocinnamic ether.

Sparingly soluble in ether.

### Oxyamidogen-nucleus $C^{18}AdH^8O^2$ .

### Carbostyryl.



L. CHIOZZA. *Compt. rend.* 34, 598; *J. pr. Chem.* 70, 278.

When nitrocinnamic acid is heated with sulphide of ammonium to the boiling point, sulphur is separated, and on supersaturating the mixture

with hydrochloric acid, a liquid, coloured brown by a resin, is produced. This liquid, when evaporated, yields crystals, which are freed from adherent resin by recrystallisation from boiling alcohol.

White silky needles. When heated, it melts to a colourless oil, which solidifies in the crystalline form on cooling, and sublimes in lustrous needles, at a higher temperature.

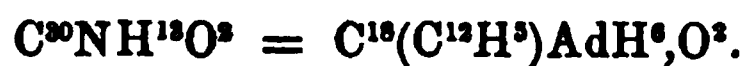
					Chiozza. mean.
18 C .....	108	....	74.5	.....	74.6
N .....	14	....	9.9	.....	10.0
7 H .....	7	....	4.9	.....	5.1
2 O .....	16	....	10.7	.....	10.3
<hr/>					
$C^{18}NH^7O^2$ .....	145	....	100.0	.....	100.0

Remains unchanged when heated with *oil of vitriol*. *Caustic potash* readily dissolves carbostyryl, and on heating a volatile base appears to be formed.

Nearly insoluble in cold, but readily soluble in boiling water. Dissolves in hydrochloric acid, not in ammonia.

*Conjugated compounds containing  $C^{18}H^6$ , or a derived nucleus.*

### Cinnanilide.



CAHOURS. *N. Ann. Chim. Phys.* 23, 344; *J. pr. Chem.* 45, 142.

*Formation and Preparation.* Aniline becomes strongly heated with chloride of cinnamyl. The resulting solid mass is repeatedly washed with water and dilute potash, and the residue dissolved in hot alcohol: cinnanilide then crystallises out on cooling.

Delicate needles, which melt at a moderate heat, and distil without decomposition at a higher temperature.

					Cahours. mean.
30 C .....	180	....	80.72	.....	80.46
N .....	14	....	6.28	....	6.41
13 H .....	13	....	5.83	.....	6.13
2 O .....	16	....	7.17	.....	7.00
<hr/>					
$C^{30}NH^{13}O^2$ .....	223	....	100.00	.....	100.00

It is scarcely attacked by potash-ley. When distilled with hydrate of potash, it decomposes into aniline and cinnamate of potash.

**Cinnanitranisidine.**

CAHOURS. *N. Ann. Chim. Phys.* 27, 252.

*Cinnanisidide nitrique, Azoture de cinnamyle, de methyl-nitrophényle, et d'hydrogène.*

When crystals of nitranisidine are introduced into chloride of cinnamyl, hydrochloric acid is liberated, and a solid mass is formed which may be purified like benzonitranisidine.

Crystallises from hot alcohol in yellowish needles.

				Cahours.
32 C	.....	192	.... 64.43	..... 64.52
2 N	.....	28	.... 9.39	
14 H	.....	14	.... 4.69	..... 4.82
8 O	.....	64	.... 21.49	
<hr/>				
$C^{32}N^2H^{14}O^8$	....	298	.... 100.00	

It is therefore cinnamate of nitranisidine *minus* 2HO (Cahours.)

**Hydrocinnamide.**

DUMAS & PELIGOT. *Ann. Chim. Phys.* 57, 325.

LAURENT. *Rev. scient.* 10, 119; *J. pr. Chem.* 27, 309.

BERZELIUS. *Jahresber.* 23, 442.

CAHOURS. *Compt. rend.* 25, 458.

*Hydrure d'azocinnamyle, Cinnhydramide, Cinnamyl-subnitrür.*

Oil of cinnamon recently prepared from Ceylon cinnamon, is treated with dry ammonia, and the viscid product is dissolved in ether-alcohol, from which beautiful crystals of hydrocinnamide crystallise on cooling: they are purified by recrystallisation. (Laurent.)

*Properties.* Colourless, rectangular prisms. (Laurent.) Lustrous silky tufts. (Dumas and Peligot.) The base is replaced by two rectangular faces, intersecting at a very obtuse angle. Melts and solidifies on cooling, to a transparent, gummy, non-crystalline mass. (Laurent.) Permanent in the air. (Dumas and Peligot.)

				Laurent.
54 C	.....	324	.... 86.17	..... 85.4
2 N	.....	28	.... 7.44	..... 7.6
24 H	.....	24	.... 6.39	..... 6.5
<hr/>				
$C^{54}N^2H^{24}$	.....	376	.... 100.00	..... 99.5

According to Dumas and Peligot, it is  $C^{18}H^{15}O^2, NH^3$  and contains 11.0 p. c. ammonia, inasmuch as these chemists found that 100 parts of oil of cinnamon take up 12.3 parts (11.56 Mulder) of ammonia.

*Decompositions.* 1. It is decomposed by dry distillation, yielding an oil and a solid substance. (Laurent.) — 2. Not decomposed by *water*. (Dumas and Peligot.) — 3. When dissolved in alcohol, it is changed by *sulphuretted hydrogen* into thiocinnol. (Cahours.) — 4. It is not altered by boiling *hydrochloric acid*, or boiling alcoholic *potash*. (Laurent.) — 5. Decomposed by boiling *nitric acid*, yielding a substance which melts in boiling water. (Laurent.)

Dissolves in *alcohol* and in *ether*, and crystallises out on cooling. (Dumas and Peligot.)

### Triphenylamine or Bicinnamylamine.



GÖSSMANN. *Ann. Pharm.* 100, 57; *J. pr. Chem.* 70, 288.

According to Gössmann, it is triphenylamine =  $(C^{12}H^5)^3 N$ . (See xi, 334.)

*Preparation.* Recently prepared bisulphite of cinnamic aldehyde-ammonia is distilled with lime, and by careful heating, a dark yellow, oily and aqueous distillate is obtained. This liquid is boiled with dilute aqueous potash, or carbonate of soda in order to remove the ammonia and the hydrocarbons; freed from alkali by repeated washings with continually smaller quantities of hot water; dried as far as possible, and heated in a stream of hydrogen, at first to remove the last traces of water; and then distilled, the temperature being kept at  $140^\circ - 150^\circ$  as long as possible. If the temperature were raised to strong ebullition, decomposition would ensue.

*Properties.* Colourless oil, heavier than water. Smells feebly of oil of cinnamon. Has an alkaline reaction.

*Decompositions.* 1. In moist air it becomes yellow, then reddish, owing to the formation of a red colouring matter very difficult to remove. — 2. Dissolves readily in iodide of ethyl, with slight rise of temperature; after 24 hours, the liquid becomes filled with large crystalline plates, which decompose after a few days, the liquor then becoming turbid, and depositing hydrate of ethyltriphenylamine (or ethylbicinnamylamine) as a red oil.

*Combinations.* Dissolves with difficulty in water. The salts, with the exception of the platinum double salt, readily change in the air, especially in aqueous or alcoholic solution, a red colouring matter being formed.

*Hydrochlorate of Bicinnamylamine.* — Concentrated hydrochloric acid does not alter colourless bicinnamylamine; alcohol of 95 per cent. causes the mixture to solidify to a colourless mass of crystals, which must be washed with alcohol.

Lustrous, somewhat reddish laminæ. Not very changeable when moist air is excluded.

When dissolved in water, alcohol or ether, it rapidly changes, and then crystallises only after being evaporated in vacuo over oil of vitriol.

Dissolves easily in water and alcohol, less readily in anhydrous alcohol and ether. When ether containing alcohol is poured on it, it is deposited as an oil, and dissolved on the addition of alcohol.

The *Chloromercurate* crystallises in laminæ and decomposes on being recrystallised.

Bicinnamylamine forms with nitrate of silver, a whitish yellow compound, which presents but little appearance of crystallisation, and soon acquires a chestnut-brown colour, probably from adhering cinnamic aldehyde.

*Bichloride of Platinum with Bicinnamylmine.* When neutral alcoholic bichloride of platinum is added to aqueous bicinnamylamine, a bright chestnut-brown, bulky, granular, crystalline salt precipitates. When freshly precipitated, it readily attracts moisture, but is permanent in the air after drying. Heated with soda-lime, it is but partially decomposed, with formation of ammonia. Dissolves readily in alcohol and in water.

Gössmann.					
36 C .....	216	...	52.08	.....	52.22
N .....	14	...	3.38		
15 H .....	15	...	3.62		
Pt .....	99	...	23.80		
2 Cl .....	70	...	17.12		
<hr/>					
$C^{36}NH^{15}, PtCl^2$ .....	414	...	100.00		

*Chloroplatinate of Bicinnamylamine.* — When an alcoholic solution of bicinnamylamine is mixed with a recently prepared and moderately strong alcoholic solution of bichloride of platinum, dark yellow bulky flakes are precipitated, which may be washed with ether. (If washed with alcohol, the flakes cake together to a resinous mass.)

Crystallises from an alcoholic solution on evaporation over oil of vitriol, in chestnut-brown crystals belonging to the regular system, which attain the size of 0.3 to 0.5 m.m., and have a glassy lustre. It is permanent in the air after drying, provided no excess of bichloride of platinum adheres to it.

Gössmann.					
36 C .....	216	...	47.88	.....	47.49
N .....	14	...	3.10		
16 H .....	16	...	3.55	.....	3.51
Pt .....	99	...	21.86	.....	22.18
3 Cl .....	106.5	...	23.61	.....	23.50
<hr/>					
$C^{36}NH^{15}, HCl + PtCl^2$ .....	451.5	...	100.00		

*Oxalate of Bicinnamylamine.* — Deliquescent needles obtained by dissolving bicinnamylamine in alcoholic oxalic acid, and repeated crystallisation from alcohol.

## Ethylbicinnamylamine.



GÖSSMANN. *Ann. Pharm.* 100, 65.

According to Gössmann, it is the hydrated oxide of ethyltriphenylammonium =  $\text{C}^{40}\text{NH}^{20}\text{O}, \text{HO}$ . (See xi, 336.)

Bicinnamylamine is enclosed with excess of iodide of ethyl in glass tubes, and the mixture left for several weeks or heated in the water-bath, until the crystalline mass, which is at first formed, disappears, and an oily layer which separates and floats on the surface, no longer increases. The tubes are then opened, the contents dissolved in alcohol, the strongly acid solution digested with excess of oxide of silver, and filtered, and the dissolved oxide of silver, precipitated by a little hydrochloric acid. When a little water is added to the alcoholic solution, the base is deposited as an oil; but when the alcoholic solution is poured into a large quantity of water, the solution merely becomes turbid, owing to the presence of certain hydrocarbons which may be removed by filtration through a wet filter.

Inodorous oil having a strong and pleasantly bitter taste, and a strong alkaline reaction.

Dissolves with some difficulty in water; the solution deposits oil-drops when boiled.

The salts of ethylbicinnamylamine are deliquescent. The base dissolves oxide of silver.

*Platinum Salt.* — Neutral bichloride of platinum precipitates from hydrochlorate of ethylbicinnamylamine, an abundant cream-coloured crystalline precipitate; the filtered solution, if rapidly concentrated, deposits yellowish red, lustrous plates.

When boiled with a quantity of water insufficient for its solution, it melts to a resin. The solution slowly evaporated deposits dark brick-red, regular crystals of a glassy lustre, which at  $90^\circ$ — $100^\circ$  become darker and lose their lustre, and then experience no further change at  $120^\circ$ .

						Gössmann.
40 C	.....	240	....	50.08	.....	49.96
N	.....	14	....	2.92	.....	2.91
20 H	.....	20	....	4.17	.....	4.25
Pt	.....	99	....	20.60	.....	20.78
3 Cl	.....	106.5	....	22.23	.....	21.80
<hr/>						
$\text{C}^{40}\text{NH}^{19}, \text{HCl} + \text{PtCl}^2$	.....	479.5	....	100.00	.....	99.70

Ethylbicinnamylamine dissolves easily in alcohol.

*Primary Nucleus  $C^{18}H^{10}$ .***Phloretic Acid.**

HLASIWETZ. (1855.) *Wien. Akad. Ber.* 17, 382; *J. pr. Chem.* 67, 105; abstr. *Ann. Pharm.* 96, 118; *J. pr. Chem.* 69, 107; *Ann. Pharm.* 102, 145; *Wien. Akad. Ber.* 24, 237; *Chem. Centralbl.* 1857, 721; *J. pr. Chem.* 72, 395.

*Preparation.* Phloretin is dissolved in so much potash-ley of sp. gr. 1.25, that there shall be about 200 c.c. of liquid to half an ounce of phloretin, and the solution is concentrated by boiling, until the mass becomes thick and gelatinous. This is dissolved, treated with carbonic acid, and again evaporated; the residue is boiled with alcohol; and the solution, which has become clear by standing and has been poured off from some phloroglucate of potash which separates as an oil, is mixed with ether, whereupon phloretate of potash separates as an oily layer at the bottom. The supernatant ether is decanted; the phloretate of potash dissolved in water; the last traces of ether are expelled by boiling; and the solution, again evaporated to a syrup and cooled, is mixed with a large excess of hydrochloric acid, whereupon it solidifies to a crystalline magma, which is purified by pressing, recrystallising from strong alcohol, which leaves chloride of potassium, and then from water to which a little animal charcoal has been added:



The phloroglucin which forms at the same time, remains with the carbonate of potash, if the above-named quantity of potash has been taken. With less potash, alcohol would dissolve some of it.

*Properties.* Crystallised from water, it forms brittle prisms belonging to the oblique prismatic system, an inch long, and with non-reflecting faces; crystallised from ether it forms thick crystals an inch long and half an inch broad, with imperfectly reflecting faces. Crystalline system, the oblique prismatic.  $oP. \infty P \infty. - P \infty. + \frac{2}{3} P \infty. [P \infty] + P u. n. - P \infty : \infty P m = 138^\circ 51'; + \frac{5}{3} P \infty : \infty P \infty = 143^\circ 19'; [P \infty] : oP = 114^\circ, 15'.$

Melts at  $128-130^\circ$  without loss of weight, and becomes crystalline on solidifying. Permanent in the air. Has a bitter, astringent taste, and strong acid reaction.

					Hlasiwetz. mean.
18 C .....	108	....	65.06	.....	64.93
10 H .....	10	....	6.02	.....	6.25
6 O .....	48	....	28.92	.....	28.82
<hr/>					
$C^{18}H^{10}O^6$ .....	166	....	100.00	.....	100.00

Hlasiwetz first gave the formula  $C^{18}H^{11}O^6$ , which Gerhardt (*Traité* 4, 1068), and Hlasiwetz himself afterwards, changed to  $C^{18}H^{10}O^6$ . (See also *Lieb. Kopp, Jahresber.* 1857, 327, and Wurtz, *N. Ann. Chim. Phys.* 52, 336.) Homologous with salicylic acid.

**Decompositions.** 1. When *heated*, it gives off suffocating odours, burns, and leaves very little charcoal. — 2. With *bromine* it forms bibromophloretic acid. — 3. Pulverised phloretic acid placed in a flask filled with *chlorine*, melts, with disengagement of heat, the colour of the chlorine disappearing, and hydrochloric acid appearing in its place. The product dissolves in alcohol and in ether, but not in water; the solution when evaporated, leaves a soft, sticky mass, which forms with soda a compound solidifying after some time to a deliquescent crystalline mass. — 4. With hydrochloric acid and *chlorate of potash*, it assumes at first a reddish brown colour, gives off abundance of gas when heated, again becomes yellow, and partially changes into yellow flakes. — 5. Triturated with *pentachloride of phosphorus*, phloretic acid becomes warm and liquid, and gives off much hydrochloric acid gas with effervescence. On distillation, oxychloride of phosphorus passes over at 100°, and a fuming liquid remains, which decomposes with water, into phloretic acid, hydrochloric acid, and phosphoric acid, and at a higher temperature becomes brown, froths up, and gives off a small quantity of oxychloride of phosphorus, leaving charcoal as a residue. — 6. When concentrated *nitric acid* is poured on phloretic acid, it dissolves, forming a red solution, with disengagement of heat, intumescence, and liberation of red vapours; the solution on cooling becomes filled with yellow crystals of binitrophloretic acid. If the temperature be not kept down, oxalic acid is also formed. — Powdered phloretic acid gradually added to cold concentrated nitric acid, dissolves without formation of red vapours, and after some time binitrophloretic acid crystallises out. If nitric acid be added to warm aqueous phloretic acid, effervescence takes place, hyponitric acid is disengaged, the liquid becomes coloured, and brown resinous drops separate, which by continued heating with addition of a little nitric acid, disappear, while binitrophloretic acid crystallises out after a little while. — 7. Phloretate of baryta mixed with *caustic lime* and a little powdered glass, and heated, yields phloretol as a brown oily distillate:



The same compound is obtained by distilling phloretate of lime with formiate of lime. — 8. With *chloride of acetyl* (or chloride of butyryl or chloride of benzoyl) it gives off hydrochloric acid and forms peculiar acids.

**Combinations.** *With water.* Phloretic acid is somewhat less soluble in water than in alcohol. The solution may be boiled continuously without decomposition. With ammonia it assumes a reddish colour in the air; with solution of hypochlorite of lime, it becomes transiently reddish brown; with sesquichloride of iron, green. The solution supersaturated with ammonia reduces nitrate of silver on the application of heat.

Phloretic acid is bibasic. It forms neutral (semi-acid) salts  $\text{C}^{18}\text{H}^8\text{M}^2\text{O}^6$ , and acid (mono-)salts  $\text{C}^{18}\text{H}^9\text{MO}^6$ . Hlasiwetz writes the semi-acid salts  $\text{C}^{18}\text{H}^9\text{O}^5, 2\text{MO}$  and assumes that they contain no water; but it appears more probable and more in accordance with the salicylates, to write them  $\text{C}^{18}\text{H}^8\text{O}^4, 2\text{MO}$  and to assume 1 atom of water in them. Moreover this may be Hlasiwetz's view (*J. pr. Chem.* 72, 402) which is supported by his statements respecting the water of crystallisation of the copper and baryta salts.

Phloretic acid readily decomposes carbonates, mostly forming acid-salts. The phloretates are all crystallisable. The acid-salts have a neutral, the neutral salts an alkaline reaction. When heated, they emit the odour of carbolic acid.



*Phloretate of Potash. — Neutral.* — 1. Obtained from carbonate of potash and aqueous phloretic acid. — 2. Aqueous phloretic acid is mixed with potash-ley, the liquid saturated with carbonic acid and evaporated; the dry mass exhausted with strong alcohol; and the resulting salt purified by pressure and recrystallisation. By spontaneous evaporation of the alcoholic solution, it is obtained in colourless radiating laminae, or tolerably large prisms. Has a warm, saline taste. Effloresces in the air. At  $100^{\circ}$  it gives off its water of crystallisation completely. Its alkaline solution becomes brown when exposed to the air.

	At $100^{\circ}$ .		Hlasiwetz.	
18 C .....	108	...	52.88	52.36
9 H .....	9	...	4.40	4.91
5 O .....	40	...	19.59	19.99
KO .....	47.2	...	23.13	22.74
<hr/>				
$C^{18}H^9KO^6$ .....	204.2	...	100.00	100.00

*Phloretate of Soda. — Acid.* — Prepared like the potash-salt. Crystallises from the very concentrated solution, which easily becomes reddish in the air, in radiating prisms which effloresce on exposure to the air.

	At $100^{\circ}$ .		Hlasiwetz.	
$C^{18}H^9O^6$ .....	157	...	83.51	
NaO .....	31	...	16.49	16.15
<hr/>				
$C^{18}H^9NaO^6$ .....	188	...	100.00	

*Phloretate of Baryta. — a. Neutral.* — Very concentrated baryta-water precipitates from a boiling solution of *b*, a bulky precipitate, which when quickly pressed and recrystallised from boiling water, is obtained in nodules. It has an alkaline reaction and is decomposed by carbonic acid. At  $100^{\circ}$  it contains 4 At. (*Ann. Pharm.* 102, 149) [5 At. (*J. pr. Chem.* 72, 402)] water of crystallisation, which are given off at  $160^{\circ}$ .

	At $100^{\circ}$ .		Hlasiwetz.	
18 C .....	108	...	31.19	31.60
13 H .....	13	...	3.75	3.81
9 O .....	72	...	20.81	20.33
2 BaO .....	153.2	...	44.25	44.26
<hr/>				
$C^{18}H^8Ba^2O^6 + 5Aq$ ....	346.2	...	100.00	100.00

	Dried at $100^{\circ}$ ( $160^{\circ}$ ?).		Hlasiwetz.	
18 C .....	108	...	34.81	34.40
9 H .....	9	...	2.91	3.00
5 O .....	40	...	12.88	13.03
2 BaO .....	153.2	...	49.40	49.57
<hr/>				
$C^{18}H^8Ba^2O^6 + Aq$ .....	310.2	...	100.00	100.00

*b. Acid.* — The aqueous solution of phloretic acid is warmed and saturated with carbonate of baryta. Beautiful, long, flat, transparent prisms, which become dull at  $100^{\circ}$ .

At 100°.				Hlasiwetz.
18 C	.....	108	... 46.23	..... 46.08
9 H	.....	9	... 3.85	..... 4.14
5 O	.....	40	... 17.13	..... 17.46
BaO	.....	76.6	... 32.79	..... 32.32
<hr/>				
$C^{18}H^9BaO^6$	.....	233.6	... 100.00	..... 100.00

*Phloretate of Lime. — Acid.* — Precipitated when a solution of lime in sugar-water is added to a concentrated aqueous solution of acid phloretate of lime until it exhibits alkaline reaction. Crystallises in vacuo in white laminæ, having an alkaline reaction. It is decomposed by carbonic acid.

*Phloretate of Magnesia.* — From carbonate of magnesia and solution of phloretic acid. Colourless crystalline geodes resembling wavellite.

*Phloretate of Zinc. — a. Neutral.* — Appears to be formed as an insoluble precipitate when phloretic acid is boiled with excess of carbonate of zinc, and remains undissolved, while *b* passes into solution.

*b. Acid.* — Obtained like the baryta-salt. Crystallises immediately from a solution filtered at the boiling heat, in flat prisms and laminæ of a velvety lustre, and resembling cholesterin. Permanent in the air. Very sparingly soluble.

At 100°.				Hlasiwetz.
18 C	.....	108	... 54.68	..... 54.47
9 H	.....	9	... 4.56	..... 5.04
5 O	.....	40	... 20.25	
ZnO	.....	40.5	... 20.51	
<hr/>				
$C^{18}H^9ZnO^6$	.....	197.5	... 100.00	

*Phloretate of Lead.* — Aqueous phloretic acid precipitates basic acetate of lead.

*a. Neutral.* — Phloretic acid is saturated with carbonate of lead, the liquid filtered, and the hot solution mixed with basic acetate of lead, by which a heavy bulky precipitate is formed. This is rapidly filtered off, and washed. It is somewhat decomposed during washing. When differently prepared, it has a somewhat different composition.

At 100°.				Hlasiwetz. mean.
18 C	.....	108	... 28.39	..... 27.26
9 H	.....	9	... 2.37	..... 2.92
5 O	.....	40	... 10.52	..... 11.53
2 PbO	.....	223.6	... 58.72	..... 58.29
<hr/>				
$C^{18}H^9Pb^2O^6 + Aq$	.....	380.6	... 100.00	..... 100.00

According to Hlasiwetz, it is  $C^{18}H^9O^6, 2PbO$ .

*b. Sesquibasic.* — In the cold, basic acetate of lead precipitates from a solution of phloretic acid which has been saturated with carbonate of lead, a salt richer in oxide of lead, very nearly corresponding to the formula  $C^{18}H^9O^6, 3PbO + 2Aq$ .

*Phloretate of Copper.* — *a. Neutral.* — When the ethereal solution of *b* is continuously warmed, or boiled, this salt separates in beautiful lustrous bluish green spangles. Dried at  $100^{\circ}$ , it contains 31.97 p. c. CuO, and is therefore  $C^{18}H^8Cu^2O^6 + 2Aq.$  [ $C^{18}H^8O^5, 2CuO + Aq.$  (*Ann. Pharm.* 102, 150);  $C^{18}H^8O^4, 2CuO + Aq.$  (*J. pr. Chem.* 72, 403), Hlasiwetz], which requires 32.29 per cent. CuO.

At 120°.				Hlasiwetz.	
18 C	.....	108	...	45.65	..... 45.51
9 H	.....	9	...	3.80	..... 4.10
5 O	.....	40	...	16.91	
2 CuO	.....	79.6	...	33.64	
<hr/>					
C <sup>18</sup> H <sup>8</sup> Cu <sup>2</sup> O <sup>6</sup> + Aq.....		236.6	...	100.00	

According to Hlasiwetz, it is  $C^{18}H^8O^5, 2CuO$  at  $120^{\circ}$ .

*b.* Prepared like salicylate of copper *b* (xii, 253.)

Emerald-green crystals, which lose 8.56 p. c. of water at  $100^{\circ}$  (2At. = 8.38 p. c.) Sparingly soluble in water and alcohol; readily soluble in ether with intense emerald-green colour.

				Hlasiwetz.		
18 C	.....	108	....	54.91	.....	54.88
9 H	.....	9	....	4.57	.....	4.89
5 O	.....	40	....	20.34	.....	19.72
CuO	.....	39.8	....	20.18	.....	20.51
<hr/>						
C <sup>18</sup> H <sup>9</sup> CuO <sup>6</sup>	.....	196.8	....	100.00	.....	100.00

*Mercurous Phloretate.* — Phloretic acid gives with mercurous nitrate a crystalline precipitate consisting of needles.

*Mercuric Phloretate.* — Neutral mercuric nitrate forms a crystalline precipitate with solutions of phloretic acid. Transparent tables.

*Phloretate of Silver.* — *Acid.* — Phloretate of soda is precipitated by nitrate of silver. The liquid solidifies to a crystalline magma, which must be filtered in the dark, washed with cold water, and then dried, first between paper, and afterwards at  $100^{\circ}$ .

Dazzling white needles, which when moist blacken readily in the light. Dissolves easily in ammonia and in acetic acid.

					Hlasiwetz.
18 C	.....	108	...	39.54	..... 39.11
9 H	.....	9	...	3.29	..... 3.33
5 O	.....	40	...	14.64	..... 14.78
AgO	.....	116.1	...	42.53	..... 42.78
<hr/>					
C <sup>18</sup> H <sup>9</sup> AgO <sup>6</sup>	.....	273.1	...	100.00	..... 100.00

*Phloretate of Urea.* — Obtained crystallised from a solution of 3 parts of urea and 1 part of phloretic acid.

Broad lustrous laminæ, or feathery striated crystals.

				Hlasiwetz.
38 C .....	228	....	58.16	..... 58.84
2 N .....	28	....	7.14	
24 H .....	24	....	6.01	..... 6.42
14 O .....	112	....	28.69	
<hr/>				
$2C^{18}H^{10}O^6, C^2N^2H^4O^2$ .....	392	....	100.00	

Hlasiwetz originally gave the formula  $2(C^{18}H^{10}O^6), C^2H^4N^2O^2, HO$ ; but according to the correction which he afterwards made in the composition of phloretic acid, the above appears the more probable.

### Sulphophloretic Acid.



NACHBAUR. *Wien. Akad. Ber.* 30, 122; *Chem. Centr.* 1858, 593.

#### *Phloretinschwefelsäure.*

*Preparation.* Vapour of anhydrous sulphuric acid is passed over pulverised phloretic acid placed in a flask, which is kept cool, until it is converted into a soft, pasty mass. This is treated with cold water which leaves the unchanged phloretic acid, and the liquid is filtered and saturated with carbonate of baryta. The solution of sulphophloretate of baryta filtered from the sulphate and from the excess of carbonate of baryta, is decomposed by sulphuric acid; the excess of sulphuric acid is removed by carbonate of lead; and the small quantity of oxide of lead which dissolves is removed by sulphuretted hydrogen. The solution filtered from the precipitates is evaporated in the water-bath, whereupon sulphophloretic acid remains as a faintly coloured very acid syrup, which crystallises with difficulty.

Dissolves very readily in water.

Sulphophloretic acid is bibasic. It forms neutral (semi-acid) and acid (mono-acid) salts. The neutral salts have alone been investigated.

*Sulphophloretate of Soda. — Neutral.* — The solution of sulphophloretate of baryta is decomposed by sulphate of soda; on evaporating the filtered solution, the sulphophloretate is obtained in faintly yellowish, crystalline crusts.

Loses its water of crystallisation completely at  $200^{\circ}$ . Dissolves easily in water, but not in alcohol or ether.

				Nachbaur.
18 C .....	108	....	37.24	..... 37.34
8 H .....	8	....	2.76	..... 2.99
2 S .....	32	....	11.04	
2 NaO .....	62	....	21.38	..... 21.30
10 O .....	80	....	27.58	
<hr/>				
$C^{18}H^8Na^2O^6, 2SO^2$ ....	290	....	100.00	

*Sulphophloretate of Baryta. — Neutral.* — Crystallises on evaporating the solution, in tolerably large, hard crystals, which are probably rhom-

bohedral. Contains 12·4 per cent. of water = 6 At. (calculation 11·2 per cent.) which are completely given off only at  $160^{\circ}$ .

Does not dissolve in alcohol or ether.

					Nachbaur.
18 C	.....	108	....	28·33	..... 25·60
8 H	.....	8	....	2·09	..... 3·31
2 S	.....	32	....	8·36	
2 BaO	.....	152·2	....	40·18	..... 39·92
10 O	.....	80	....	21·04	
<hr/>					
$C^{18}H^{10}Ba^2O^6, 2SO^3$ ....					380·2 .... 100·00

*Sulphophloretate of Lime. — Neutral.* — Obtained by saturating phloretic acid with carbonate of lime, and remains as a crystalline mass when the solution is evaporated.

Dried in the air, it contains 20·7 p. c. of water, which are given off at  $170^{\circ}$  = 8 At. (Calculation = 18·3 per cent.)

					Nachbaur.
At $170^{\circ}$ .					
18 C	.....	108	....	38·02	..... 38·22
8 H	.....	8	....	2·81	..... 3·00
2 S	.....	32	....	11·29	
2 CaO	.....	56	....	19·71	..... 19·85
10 O	.....	80	....	28·17	
<hr/>					
$C^{18}H^{10}Ca^2O^6, 2SO^3$ ....					284 .... 100·00

*Sulphophloretate of Magnesia.* — The solution obtained by saturating sulphophloretic acid with carbonate of magnesia, leaves on evaporation in the air a gummy mass, which afterwards becomes hard and pulverisable. Contains 11·02 per cent. water = 4 At. Calculation = 11·84 per cent.

					Nachbaur.
18 C	.....	108	....	40·29	..... 40·56
8 H	.....	8	....	2·98	..... 3·38
2 S	.....	32	....	11·96	
2 MgO	.....	40	....	14·92	..... 15·08
10 O	.....	80	....	29·85	
<hr/>					
$C^{18}H^{10}Mg^2O^6, 2SO^3$ ....					268 .... 100·00

Sulphophloretic acid dissolves very readily in *alcohol*.

### Ethylphloretic Acid.



HLASIWETZ. *Ann. Pharm.* 102, 151.

*Phloretate of ethyl, Acid phloretic ether.*

Phloretate of potash (or of silver) is heated with excess of iodide of ethyl and a little alcohol in a closed tube for some hours in the water-bath. When almost all the iodide of potassium has separated from the

mixture, which at first is quite homogeneous, the faintly yellowish liquid is heated in the water-bath to drive off the alcohol and excess of iodide of ethyl; the residue heated in the oil-bath to 230° or 240° to volatilise all foreign matters, then distilled over the open flame; and the distillate is agitated with silver and rectified.

Colourless, viscous. Does not boil at 265°. Faint smell and grating taste. Makes oil-spots upon paper.

						Hlasiwetz.
22 C	.....	132	....	68·04	.....	68·15
14 H	.....	14	....	7·22	.....	7·55
6 O	.....	48	....	24·74	.....	24·30
<hr/>						
C <sup>22</sup> H <sup>14</sup> O <sup>6</sup>	.....	194	....	100·00	.....	100·00

Cannot be set on fire. Heated on platinum, it gives off suffocating odours. In contact with ammonia it forms phloretamic acid. With nitric acid it forms ethylbinitrophloretic acid.

Dissolves in alcohol and ether, and is precipitated from the solutions by water.

### Amylphloretic Acid.



HLASIWETZ. *Ann. Pharm.* 102, 154; *J. pr. Chem.* 72, 407.

*Phloretate of amyl.*

*Preparation.* Very concentrated alcoholic phloretate of potash is heated with iodide of amyl in the oil-bath for a long time to boiling; the liquid when cool is poured off from the iodide of potassium and heated to 140° as long as anything passes over; and the residue is treated with warm water, which dissolves iodide of potassium, and deposits amylophloretic acid as a coloured heavy oil. The water is expelled from this product by heating, a small quantity of iodine is removed by silver; the liquid is heated for some time to 140° until nothing more passes over; and the residue is distilled over the open fire in a bent, sharply inclined tube.

Colourless, very viscid. Feeble, rancid odour. Sharp, biting taste. Boiling point above 290°.

					Hlasiwetz.
28 C	.....	168	...	71·18	..... 71·42
20 H	.....	20	...	8·47	..... 8·43
6 O	.....	48	...	20·35	..... 20·15
<hr/>					
C <sup>28</sup> H <sup>20</sup> O <sup>6</sup>	.....	236	...	100·00	..... 100·00

By *nitric acid* it is converted into a crystalline compound like ethylbinitrophloretic acid.

Dissolves in alcohol and ether like ethylphloretic acid.

*Appendix.***Phloretol.**HLASIWETZ. *Ann. Pharm.* 102, 166.

A mixture of phloretate of baryta with caustic lime and a little powdered glass is distilled in small portions over the open fire, and the brown oily distillate is dehydrated by decantation and drying over oil of vitriol, and then rectified.

Colourless, strongly refracting oil, which becomes thicker at  $18^\circ$ , and boils at  $190^\circ - 200^\circ$ . Sp. gr. 1.0374 at  $12^\circ$ . Has an aromatic odour, suggestive of carbolic acid, and a burning taste. Placed on the skin it causes a burn. Coagulates albumen almost as rapidly as carbolic acid. A splinter of pine-wood dipped in aqueous phloretol, and then soaked with hydrochloric acid, assumes, when dried in the sun, a colour similar to that produced in like manner by carbolic acid. Vapour densit = 4.22.

				Hlasiwetz.
16 C .....	96	...	78.68	78.70
10 H .....	10	...	8.19	8.17
2 O .....	16	...	13.13	13.13
<hr/>				
$C^{16}H^{10}O^2$ .....	122	...	100.00	100 00

	Vol.	Density.
C-vapour .....	16	6.6560
H-gas .....	10	0.6930
O-gas .....	1	1.1093
<hr/>		
Vapour of phloretol .....	2	8.4583
	1	4.2291

Isomeric with phenetol. Stands in the same relation to phloretic acid, as carbolic acid to salicylic acid.

*Decompositions.* 1. In vessels containing *air*, it becomes yellowish and then smells of styrol. — 2. When soaked up into a wick, it may be set on fire, and then *burns* with a bright, fuliginous flame. — 3. Dissolves in *oil of vitriol*; the solution, after standing some time, is no longer precipitated by water, but then contains a conjugated sulphuric acid compound, which forms with baryta a soluble easily crystallisable salt. — 4. When *bromine* is poured on it, hydrobromic acid is liberated, and after the excess of bromine is expelled, a white crystalline substitution-product is left, which is soluble in alcohol, but not in water. — 5. With *chlorine* it forms a substitution-product. — 6. With *nitric acid* it hisses like a red-hot metal, and forms ternitrophloretol with violent action and disengagement of hyponitric acid.

Phloretol is but sparingly soluble in *water*. It mixes with *alcohol*, and *ether* in all proportions.

## Ternitrophloretol.



ASIWETZ. *Ann. Pharm.* 102, 167.

Phloretol is carefully dropped into strong nitric acid; the mixture is heated until the resinous drops disappear; and the resulting crystals after being heated for some hours, are washed with cold water, and crystallised from alcohol. Contains 15.56 p. c. N. (Calculation 16.34 p. c.)

Oxygen-nucleus  $\text{C}^{18}\text{H}^8\text{O}^3$ .

## Cumariic Acid.



DELALANDE. *N. Ann. Chim. Phys.* 6, 343; *J. pr. Chem.* 28, 356; *Ann. Pharm.* 45, 332.

BLEIBTREU. *Ann. Pharm.* 59, 183.

*Cumarinsäure, Cumarsäure, Acide cumarique.*

*Preparation.* Cumarin is boiled with concentrated potash-ley (to which sticks of hydrate of potash are added: Bleibtren); the mass is dissolved in water, and the cumariic acid is precipitated by a stronger acid. (Delalande.)

Bleibtren frees the cumariic acid from a small quantity of salicylic acid formed at the same time, by recrystallisation from boiling water and washing with cold water, until the liquid which drops through, no longer colours ferric salts violet. In order to remove any cumarin which is still undecomposed, he dissolves the acid in ammonia; expels the excess of ammonia by boiling; precipitates by nitrate of silver; collects the yellowish white precipitate; washes it with water, and then with alcohol and ether; decomposes it with hydrochloric acid; extracts the cumariic acid with ether; evaporates the ether; and recrystallises the acid from boiling water.

*Properties.* Transparent laminæ having a strong lustre. (Delalande.) Brittle. Melts towards 190°. (Bleibtren.) Has a bitter taste. (Delalande.) Reddens litmus.

At 100°.				Delalande.		Bleibtren.	
18 C	.....	108	...	65·85	.....	65·34	... 65·61
8 H	.....	8	...	4·88	.....	5·03	... 4·98
6 O	.....	48	...	29·27	.....	29·63	... 29·41
<hr/>							
C <sup>18</sup> H <sup>8</sup> O <sup>6</sup>	.....	164	...	100·00	.....	100·00	... 100·00

*Decompositions.* 1. By distillation, it yields vapours smelling like benzoic acid, together with a volatile oil, which reddens ferric salts,



combines with potash, and leaves resin as a residue. (Delalande.) Heated above  $190^\circ$  it partially decomposes, white lustrous crystals subliming, and a brown residue remaining. (Bleibtreu.)—2. By fusion with *hydrate of potash*, it is changed into *salicylic acid*:



(See below.) Acetic acid appears to be formed at the same time, probably according to the equation:



Cumaric acid dissolves in boiling water, and crystallises on cooling.

It neutralises bases completely. (Delalande.) It expels carbonic acid from carbonates. (Bleibtreu.)

It reddens ferric salts (Delalande), but only when it is contaminated with salicylic acid. (Bleibtreu.)

The ammonia-salt does not precipitate *baryta-salts*; from *acetate of lead* a white powder soluble in water is precipitated. (Bleibtreu.)

*Cumarate of Silver.*—*a.* From excess of cumarate of ammonia containing free ammonia, nitrate of silver precipitates orange-yellow flakes, which turn brown in the air, and are immediately decomposed at  $100^\circ$ . (Bleibtreu.)

*b.* The neutral ammonia-salt is precipitated by nitrate of silver. Yellowish white powder, which quickly subsides. In the air and at  $100^\circ$ , it remains unchanged. (Bleibtreu.)

					Delalande.	Bleibtreu.		
18 C	.....	108	....	39.84	.....	39.8	....	40.00
• 7 H	.....	7	....	2.58	.....	2.6	....	2.64
Ag	.....	108.1	....	39.86	.....	39.5	....	39.72
6 O	.....	48	....	17.72	.....	18.1	....	17.64
<hr/>								
C <sup>18</sup> AgH <sup>7</sup> O <sup>6</sup>	.....	271.1	....	100.00	.....	100.0	....	100.00

Cumaric acid dissolves easily in *alcohol* and *ether*. (Bleibtreu.)

### Insolinic Acid.



A. W. HOFMANN. (1856.) *Ann. Pharm.* 97, 197; abstr. *Compt. rend.* 41, 718.

*Acide cuminocymynique.* (Persoz.)

First observed by Persoz in 1842 (*Compt. rend.* 13, 433; *J. pr. Chem.* 25, 59), investigated by Hofmann.

*Formation.* By boiling Roman oil of carraway, euminol, cuminic acid or cymene with bichromate of potash and sulphuric acid.

*Preparation.* 1 part of cuminic acid, or cymene or Roman oil of carraway is heated slowly, and with good condensing apparatus, with a mixture of 1pt. bichromate of potash, 8 parts of oil of vitriol and 12 parts

of water, so that the distillate flows back, until on cooling neither oil nor crystals are deposited, but the whole is changed into pulverulent insolinic acid and semifused insolate of chromium. The mixture is filtered; the residue washed with water and boiled with ammonia; the liquid filtered from the separated oxide of chromium; and the filtrate supersaturated with hydrochloric acid: insolinic acid then separates as a white powder, and is purified by boiling with water and afterwards with alcohol. (Hofmann.) Persoz allowed a mixture of 1 part bichromate of potash, 2·2 parts oil of vitriol and 8 parts water to act on Roman oil of cumin at 60°—70°, filtered from the cuminic acid which separated and then heated the mixture to boiling: the liquid then frothed up and his *acide cumino-cyminique* was deposited.

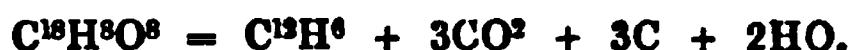
**Properties.** White powder consisting of microscopic crystals. Inodorous, tasteless. Melts at a very high temperature. Sublimes partially undecomposed. (Hofmann.) Volatile without melting. Heavier than water. (Persoz.) When dissolved in boiling water, it has a strong acid reaction. (Hofmann.)

					Hofmann.
					mean.
18 C .....	108	....	60·00	.....	59·70
8 H .....	8	....	4·44	.....	4·30
8 O .....	64	....	35·56	.....	36·00
<hr/>					
$C^{18}H^8O^8$ .....	180	....	100·00	.....	100·00

**Decompositions.** 1. It is partially decomposed by distillation, forming benzoic acid, benzol, carbonic acid and charcoal:



2. It is not changed by long boiling with *chromate of potash* and *sulphuric acid*, or by continued boiling with concentrated nitric acid. —  
3. Distilled with *caustic baryta*, it yields benzol and leaves carbonate of baryta and charcoal:



4. When it is suspended in alcohol and *hydrochloric acid gas* is passed through the liquid, or when its silver-salt is heated with iodide of ethyl in a sealed tube, it forms insolate of ethyl and ethylinsolanic acid, which are separable by potash. (Hofmann.)

**Combinations.** Insolinic acid scarcely dissolves (not at all, according to Persoz) in cold, somewhat more in boiling water, and is precipitated on cooling as an indistinct crystalline powder.

Dissolves in cold and in boiling oil of vitriol without blackening, and is precipitated unchanged by water. (Hofmann.) It is not dissolved by oil of vitriol, but after being boiled with it for a few minutes, becomes soluble in water. (Persoz.)

Insolanic acid is bibasic. It forms acid (mono-acid), neutral (semi-acid), and double salts. It completely neutralises the fixed alkalis and ammonia, and decomposes the carbonates on boiling.

**Insolate of Potash.** — *a. Neutral.* — Precipitated by strong alcohol from the saturated solution of insolinic acid in potash-ley. Crystalline powder, with a silky lustre after being dried. Decomposed by acids

with separation of 69·28 p. c. insolinic acid. (Calculation = 70·31 per cent.)

Hofmann.				
$C^{18}H^6O^3$ .....	178	...	69·54	
2 K .....	78	...	30·46	..... 30·36
<hr/>				
$C^{18}H^6K^2O^3$ ....	256	...	100·00	

*b. Acid.* — When the salt *a* is boiled with excess of insolinic acid and filtered hot, crystalline plates separate on cooling. Decomposed by acids, with elimination of 82·11 per cent. insolinic acid. ( $C^{18}H^7KO^3$  requires 82·56 per cent.)

*Insolinate of Potash and Soda.* — When the solution of the potash-salt *b* is neutralised with carbonate of soda and precipitated by alcohol, a salt precipitates, which, on being decomposed by hydrochloric acid, yields 74·47 per cent. insolinic acid. (Calculation 75·0 p. c.) Cannot be obtained by crystallisation.

Hofmann.				
$C^{18}NaH^6O^3$ .....	201	...	83·75	
K .....	39	...	16·25	..... 16·16
<hr/>				
$C^{18}H^6KNaO^3$ .....	240	...	100·00	

*Insolinate of Baryta.* — *Neutral.* — Dilute insolinate of ammonia does not precipitate baryta-salts; but if concentrated it produces a white, more or less crystalline precipitate, which, after washing with cold water and drying at 120° to 140°, yields 56·74 per cent. insolinic acid when decomposed by hydrochloric acid.

Hofmann.				
$C^{18}H^6O^3$ .....	178	...	56·51	
2 Ba .....	187	...	43·49	..... 43·65
<hr/>				
$C^{18}H^6Ba^2O^3$ .....	315	...	100·00	

*Insolinate of Lime.* — *Neutral.* — Obtained like the baryta-salt, which it resembles. It loses its water at 120° — 130°, and then contains 18·67 per cent. calcium. (Calculation 18·35 per cent.)

Hofmann.				
$C^{18}H^6O^3$ .....	178	...	65·50	
2 Ca .....	40	...	14·70	.... 14·96
6 HO .....	54	...	19·80	..... 19·90
<hr/>				
$C^{18}H^6Ca^2O^3 + 6Aq$ .....	272	...	100·00	

*Insolinate of Copper* is thrown down as a bright blue precipitate on mixing neutral solutions of sulphate of copper and a salt of insolinic acid. Contains 32·57 p. c. Cu, and is probably represented by the formula  $C^{18}Cu^2H^6O^3 + CuO, HO$ , which requires 32·78 p. c. Cu.

*Insolinate of Silver.* — Precipitated from insolinate of ammonia by

nitrate of silver as a white, amorphous, curdy precipitate. It must be washed in the dark for a long time. (Hofmann.)

				Hofmann.
18 C .....	108	...	27.41	27.25
6 H .....	6	...	1.52	1.51
2 Ag.....	216	...	54.82	54.64
8 O .....	64	...	16.25	16.60
<hr/>				
C <sup>18</sup> Ag <sup>2</sup> H <sup>6</sup> O <sup>8</sup> ....	394	...	100.00	100.00

Insolinic acid is insoluble in *alcohol* (Persoz); almost insoluble. (Hofmann.) It is insoluble in *ether*.

*Oxygen-nucleus* C<sup>16</sup>H<sup>6</sup>O<sup>4</sup>.

**Cumarin.** C<sup>16</sup>H<sup>6</sup>O<sup>4</sup>.

- A. VOGEL. *Gilb.* 64, 161; *J. Pharm.* 6, 305.  
 GUIBOURT. *Drogues simples*.  
 BOULLAY & BOUTRON-CHARLARD. *J. Pharm.* 11, 480.  
 TRAUTWEIN. *Repert.* 24, 98.  
 BUCHNER. *Repert.* 24, 126.  
 GUILLEMETTE. *J. Pharm.* 21, 172; *Ann. Pharm.* 14, 324.  
 DELALANDE. *N. Ann. Chim. Phys.* 6, 343; *J. pr. Chem.* 28, 256; *Ann. Pharm.* 45, 332.  
 KOSSMANN. *N. J. Pharm.* 5, 393; *J. pr. Chem.* 33, 55; *Ann. Pharm.* 52, 387.  
 LEROY. *N. J. Pharm.* 11, 37.  
 HERRM. BLEIBTREU. *Ann. Pharm.* 59, 177.  
 GOBLEY. *N. J. Pharm.* 17, 348; *J. pr. Chem.* 50, 286.  
 A. FRAPOLLI & CHIOZZA. *Ann. Pharm.* 95, 252; *J. pr. Chem.* 66, 342.  
 GÖSSMANN. *Ann. Pharm.* 98, 66.  
 G. & C. BLEY. *N. Br. Arch.* 142, 32; *Pharm. Centr.* 1858, 827.

*Cumarine, Tonka-camphor.*

Cumarin was first remarked by Vogel (1820), who mistook it for benzoic acid; Guibourt discovered that it was a new substance; and it was more closely investigated by Delalande in 1842, and by Bleitreu in 1846.

**Sources.** Found in tonka-beans. — In *Melilotus officinalis* (Fontana, *Pharm. Centr.* 1833, 684; Chevallier & Thubeuf, *J. Chim. med.* 10, 350, Guillemette, Bleibtreu); in *Asperula odorata* (Vogel, Kossmann), and in *Anthoxanthum odoratum* (Bleibtreu); in the fruit of *Myroxylon toluiferum* (Leroy), in the leaves of *Angraecum fragrans* (Gobley), and in the herb of *Orchis fusca*. Jacq. (Bley.)

It appears that in fresh tonka-beans, the cumarin is dissolved in an oil from which it gradually separates in white crystals, which are chiefly

deposited between the outer surfaces of the cotyledons and the seed-envelopes. (Bleibtreu.)

*Preparation. a. From Tonka-beans.* 1. The powdered beans are exhausted with ether, and after the ether has been evaporated, the residual cumarin is dissolved in alcohol of  $35^{\circ}$  B. which leaves a residue of fat. The solution is then evaporated, the dirty yellow crystals thus obtained are again dissolved in alcohol; and the solution is boiled with animal charcoal, filtered and evaporated, until it begins to crystallise. (Boullay & Boutron-Charlard.) A portion of the cumarin remains with the residue of fat, from which it may with great difficulty be extracted by alcohol. (Bleibtreu.) — 2. The beans are chopped up or pulverised and exhausted with cold alcohol of  $36^{\circ}$  (Delalande), or digested with strong alcohol (Bleibtreu); the tincture is then evaporated to the consistence of syrup, and allowed to cool, and the crystals which form are purified by repeated crystallisation (Delalande), and by treatment with animal charcoal. (Bleibtreu.) — 3. Finely chopped tonka-beans are heated for a long time nearly to boiling with an equal bulk of alcohol of 80 p. c; the whole is then filtered and the residue again treated in the same manner; the extracts are mixed together and the alcohol is distilled from them till the residue grows turbid, whereupon it is mixed with four times its volume of water, which precipitates cumarin in the crystalline state. The whole is now heated to boiling and filtered through a moistened filter which retains the fat; and the filtrate is then cooled, the greater part of the cumarin crystallising out pure. The remainder is obtained by evaporating the mother-liquor and treating the resulting crystals with animal charcoal. 1 lb. of tonka-beans yields 7 grammes of cumarin. (Gössmann.) — 4. When the beans are distilled with water, the distillate deposits cumarin after 24 hours. (Boullay & Charlard.)

*b. From Melilotus, Asperula, Anthoxanthum, or Angraecum fragrans.* 1. The coarsely powdered flowers of *Melilotus* are exhausted in a digesting funnel with alcohol of  $35^{\circ}$ , and the alcohol is distilled from the yellowish green tincture until the weight of the residue is equal to half of that of the flowers employed; it is next poured into a dish; the layer of fat which forms after a time is removed; the liquid is evaporated to a syrup; the crystals which are then deposited are collected on a piece of linen; and the mother-liquor (yielding a few more crystals on further evaporation) is allowed to flow off. The residue is washed with cold water and purified by recrystallisation from boiling water and treatment with animal charcoal. (Guillemette.) — 2. Bleibtreu takes *Asperula odorata* or *Anthoxanthum odoratum*, gathered and dried shortly before or whilst it is in blossom; digests it with alcohol; distils the alcohol from the tincture (the last portion of the distillate deposits a little cumarin); boils out the residual syrupy liquid with water; filters off the chlorophyll, and shakes the filtrate with ether, which takes up the cumarin and deposits it on evaporation as a yellow residue resembling honey; and dissolves this residue in boiling water, whereupon the solution on cooling first becomes milky, and then deposits large crystals of cumarin. The crystals are obtained perfectly white by three crystallisations, but they still deposit brownish black flakes when melted: they are therefore recrystallised after melting. — In the same way, Goble extracts cumarin from *Angraecum fragrans*, and Kossmann employs a similar process in the extraction from *Asperula odorata*, using ether as well. — 3. The herb of *Orchis fusca* is bruised, the sap pressed out, and the solid portion

exhausted with alcohol of sp. gr. 0.897. The alcoholic extract is then mixed with the expressed sap; the whole purified by decantation and filtration; the alcohol distilled off; and the residue left to evaporate. In a few days, an abundant crop of crystals is formed in the syrup, which, after they have been treated with animal charcoal and recrystallised, amount to 0.25 p. c. of the fresh plant. (G. & C. Bley.)

**Properties.** Small, colourless, rectangular laminae having a silky lustre and belonging to the right prismatic system. (Fig. 55.)  $\alpha' : \alpha = 86^\circ$ ;  $i : l = 110^\circ 12'$ ;  $i : \alpha = 104^\circ 28'$ ; sometimes also thick, yellowish prisms with lateral faces  $\alpha$   $\alpha'$ , but without well defined ends. (De la Provostaye.) Very hard; cracks between the teeth. (Delalande.) Of smooth fracture. (Boullay & Charlard.) Melts at  $50^\circ$  (Buchner, Delalande); at  $40^\circ$ . (Kossmann.) Cumarin prepared from *Melilotus* or *Angræcum* does not melt below  $120^\circ$ , but that which is prepared from tonka-beans melts at a lower temperature because it contains fat. (Gobley.) Solidifies on cooling in a transparent confusedly crystalline mass; volatilises and sublimes (Boullay & Charlard) in white needles smelling of bitter almonds. (Guillemette). Boils at  $270^\circ$ . (Delalande.) Heavier than water. Neutral. Smells strongly aromatic (Boullay), like *Melilotus* (Buchner, Guillemette), and, like bitter almonds, especially when rubbed between the fingers. (Gobley.) The vapour strongly affects the brain. (Delalande.) Tastes hot and pungent (Boullay), bitter and aromatic (Buchner), fiery, like volatile oil (Delalande). Cumarin prepared from *Melilotus* and *Angræcum*, has a bitter and then pungent taste; that prepared from tonka-beans has a pure, bitter taste. (Gobley.) Cumarin in large quantities acts as a narcotic. (Bleibtren.)

				Delalande.		Bischoff.				
				mean.		a.		b.		
18 C	.....	108	...	73.97	.....	72.91	...	73.98	...	73.85
6 H	.....	6	...	4.11	.....	4.73	...	4.38	...	4.24
4 O	.....	32	...	21.92	.....	22.36	...	21.64	...	21.91
<hr/>										
C <sup>18</sup> H <sup>6</sup> O <sup>4</sup>	.....	146	...	100.00	.....	100.00	...	100.00	...	100.00
<hr/>										
				O. Henry.		Gobley.				
18 C	.....	108	...	73.97	.....	76.40	...	76.12		
6 H	.....	6	...	4.11	.....	3.99	...	4.12		
4 O	.....	32	...	21.92	.....	19.61	...	19.76		
<hr/>										
C <sup>18</sup> H <sup>6</sup> O <sup>4</sup>	.....	146	...	100.00	.....	100.00	...	100.00		

Henry (*J. Pharm.* 21, 272), Delalande and Bleibtren (b) investigated cumarin from tonka-beans; Bleibtren (a) from *Asperula odoratum*, and Gobley from *Angræcum*. Henry gave the formula  $C^{20}H^6O^4$ ; Delalande, the formula  $C^{18}H^7O^4$ ; Dumas (*Traité* 7, 163) and Bleibtren, that which is here adopted.

**Decompositions.** Vapour of cumarin takes fire in contact with flaming bodies, and burns with a white flame. (Buchner.)—2. Cumarin is immediately charred by oil of vitriol. (Delalande.)—3. Tincture of iodine converts it into a crystalline mass having a golden lustre.—4. Decomposed by bromine and chlorine, with formation of white crystalline bodies.—5. Boiling concentrated hydrochloric acid is without action upon

cumarin. (Delalande.) — 6. Cold fuming *nitric acid* converts it into nitrocumarin; if cumarin is boiled for a long time with commercial nitric acid and the distillates are poured back, it is completely converted into picric acid. (Delalande, Bleibtreu.) No oxalic acid is produced by the action of nitric acid on cumarin. (Guillemette.) — 7. Cumarin is not altered by *ammonia*, either in solution or in the gaseous state. (Delalande.) — 8. By boiling concentrated solution of potash (when the hydrate of potash begins to fuse), it is converted into cumarate of potash. Cumarin fused with hydrate of potash is converted into salicylate of potash (Delalande), with evolution of hydrogen and formation of carbonate of potash. (Bleibtreu.) According to Delalande, hydrogen is evolved in the formation of cumaric acid, and a combustible hydrocarbon  $C^4H^2$ , of aromatic odour in the conversion of the cumaric acid into salicylic acid. In the first case, Bleibtreu was unable to discover any evolution of gas, except that arising from any traces of salicylic acid that might be formed; and in the conversion of cumaric acid into salicylic acid, he only obtained hydrogen, the odour and luminous properties of which he considers to be due to an admixture of hydrate of phenyl arising from the action of the potash upon the salicylic acid. Alcoholic potash also produces cumaric acid, but more slowly, so that part of the cumarin remains undecomposed after prolonged treatment:



When cumarin is boiled with a solution of *pentachloride of antimony* in hydrochloric acid, gas is evolved and the cumarin is converted into yellow crystals containing chlorine and antimony. (Delalande.) (See below.) — 10. Cumarin when swallowed, passes unchanged into the urine. (Hallwachs, *Ann. Pharm.* 105, 210.)

*Combinations.* Cumarin is scarcely soluble in cold water, readily in boiling water. — The solution of 1 pt. of cumarin in 45 pts. of boiling water becomes milky on cooling; the solution of 1 pt. of cumarin in 200 pts. of water remains clear at  $25^\circ$ , but when slowly cooled to  $15^\circ$  yields long prisms; that of 1 pt. of cumarin in 400 pts. of water remains unchanged, even in the cold. (Buchner.) An excess of cumarin heated to boiling with water, melts to an oil which solidifies in a tolerably hard mass on cooling. Yields, when distilled with water, a distillate smelling of melilot. (Guillemette.)

Dissolves sparingly in oil of vitriol (Leroy), abundantly (Guillemette), and may be precipitated by addition of water.

Dissolves in concentrated, or in warm diluted phosphoric acid. Insoluble in cold ammonia. (Guillemette.)

Cumarin is readily dissolved by potash (without evolution of ammonia, Buchner), and forms a coloured solution from which acids precipitate cumarin unchanged. (Delalande, Bleibtreu.)

The aqueous solution of cumarin is very abundantly precipitated by subacetate of lead. (Guillemette.)

*With Terchloride of Antimony.* — A solution of pentachloride of antimony in hydrochloric acid is boiled with cumarin; on cooling, yellow crystals are deposited, which are decomposed by heat and deliquesce with water after a time. The aqueous solution of these crystals soon deposits a white powder and needles of silky lustre, which appear to be cumarin.



Calculation according to Delalande.				Delalande.	
18 C	.....	108	....	38.94	..... 34.55
7 H	.....	7	....	2.19	..... 2.60
4 C	.....	32	....	10.05	..... 6.45
$\frac{1}{2}$ Sb	.....	64.5	....	20.26	..... 22.40
3 Cl	.....	106.8	....	38.56	..... 34.00
<hr/>				<hr/>	
$C^{18}H^7O^4, Sb\frac{1}{2}Cl^3$	.....	318.3	....	100.00	..... 100.00

It is perhaps a compound of pentachloride of antimony with cumarin, containing chlorine. (Delalande.)

Cumarin dissolves much more readily in *acetic acid* (Buchner), and in *tartaric acid* (Guillemette), than in water.

Dissolves very readily in *alcohol*. — Dissolves readily both in volatile and in fatty oils. (Boullay & Charlard.)

### Purpurin.



COLIN & ROBIQUET. *Ann. Chim. Phys.* 34, 244; *J. Pharm.* 12, 407; *Berz. Jahresb.* 7, 265; *J. Pharm.* 13, 447; *Berz. Jahresb.* 8, 273.

GAULTIER DE CLAUBRY & J. PERSOZ. *Ann. Chim. Phys.* 48, 69; *N. Tr.* 25, 2, 186.

PERSOZ. *Ann. Chim. Phys.* 51, 110.

F. F. RUNGE. *J. pr. Chem.* 5, 362; *Ann. Chim. Phys.* 63, 282.

ROBIQUET. *Ann. Chim. Phys.* 63, 297.

J. SCHIEL. *Ann. Pharm.* 60, 74.

DEBUS. *Ann. Pharm.* 66, 351; 86, 117; *N. Ann. Chim. Phys.* 38, 490.

J. WOLFF & STRECKER. *Ann. Pharm.* 75, 1; *Pharm. Centr.* 1850, 593; *Chem. Soc. Qu. J.* 3, 243.

ROCHLEDER. *Wien. Akad. Ber.* 6, 433; *J. pr. Chem.* 55, 385; *Ann. Pharm.* 80, 321; *Wien. Akad. Ber.* 7, 806; *Ann. Pharm.* 82, 205; *J. pr. Chem.* 66, 85.

**Purpurin.** (Colin & Robiquet.) *Matière colorante rose*. (Gaultier de Claubry & Persoz). *Madder-purple* (Runge, Schiel). *Oxylizaric acid* (Debus). — Discovered by Colin and Robiquet in 1826, but apparently first obtained completely pure by Debus and by Wolff & Strecker; the latter also determined the formula of purpurin. According to Schunck (*Phil. Mag. J.* 5, 510; *Ann. Pharm.* 81, 349,) purpurin is a mixture of alizarin and verantin in varying proportions; Debus was, however, unable to decompose purpurin by treating its alcoholic solution with acetate of copper, whilst according to Schunck, verantin is precipitated by this treatment and alizarin remains in solution.

**Sources.** In madder-root.

**Formation.** Alizarin is converted into purpurin in the fermentation of madder. (Wolff & Strecker.) When alizarin is treated with aqueous chlorine, it seems to undergo no change; but after the chlorine has been removed, it gives with potash a deep red solution like purpurin, and with baryta a purple-red precipitate; it has therefore probably been converted into purpurin. (Wolff & Strecker.)



*Preparation.* 1. Alsace or Avignon madder is stirred up with yeast and water and allowed to ferment in a warm place out of contact with the air; when the fermentation is over, the madder is washed with water and the residue is boiled with a concentrated solution of alum which assumes a beautiful deep red colour, appearing orange-yellow by reflected light. On cooling the solution and adding sulphuric acid, it deposits red flakes of purpurin, which are freed from an admixture of small quantities of alumina by boiling with hydrochloric acid, and are then recrystallised from alcohol or ether. (Wolff & Strecker.) When Avignon madder is exhausted with boiling water, the decoction precipitated by sulphuric acid, the precipitate washed and while still moist boiled with a concentrated solution of chloride of aluminum, the colouring matters dissolve and leave a residue of dark-coloured substances. On mixing the solution with a little hydrochloric acid, fiery-red and sometimes crystalline flakes are precipitated, consisting of alizarin and purpurin which still retain resin. When the flakes are dissolved in alcohol or in dilute ammonia, and freshly precipitated hydrate of alumina, which combines with the colouring matter, is added, and the resulting compound is boiled with concentrated carbonate of soda, purpurin is dissolved with dark-red colour, while alizarin-alumina remains in the residue. It is difficult however to obtain pure purpurin from this solution. (Wolff & Strecker.)

2. Powdered madder-root is boiled with a large quantity of water to which sulphuric acid is added in the proportion of 90 grammes of acid to each kilogr. of madder, whereby the gum is soon converted into sugar and the madder may now be readily washed out with water. After the root has been thus treated and washed out, it is exhausted by twice boiling with carbonate of soda; the residue is then washed with water as long as the water becomes coloured, and the solutions are set aside for the preparation of alizarin. When the madder-root which has been exhausted with soda is boiled with a solution of alum, it yields a beautiful cherry-red extract; this is filtered and mixed with a slight excess of hydrochloric acid or sulphuric acid, whereupon a beautiful red precipitate is formed, which is collected on a filter, well washed, and purified by solution in alcohol and evaporation. (Gaultier & Persoz.) Or the madder boiled with sulphuric acid is treated with 3 p. e. of protochloride of tin and a small quantity of potash, in which the colouring matters dissolve. On adding an acid to the solution, red flakes are precipitated which are carefully washed and then treated with a solution of alum, whereupon alizarin remains undissolved but purpurin dissolves; the last solution is precipitated with sulphuric acid, and the purpurin dissolved in alcohol or in ether and crystallised by evaporation. (Gaultier & Persoz.)

3. Four pounds of Levant madder-root is coarsely chopped (the washing out of the *ground* root is troublesome and attended with loss) and macerated for 12 hours in hot water, and then thoroughly washed; by this treatment the root becomes very soft and may be easily pounded. It is next boiled with 12 lbs. of alum and 70 lbs. of water for an hour, and strained; the residue is again boiled with 6 lbs. of alum and 70 lbs. of water for half an hour; the liquid is again strained; and the united extracts are set aside for four days in order that they may deposit. The madder-root which has been twice boiled may be boiled a third time with 70 lbs. of water, and this decoction used for extracting fresh root. On mixing the decanted alum solution, which is of a beautiful rose-colour, with 3 lbs. of sulphuric acid and 9 lbs. of water, it deposits yellowish red flakes and becomes pale yellow. The whole is allowed to stand for several days, then filtered, and the residue

is collected, whereby  $\frac{1}{2}$  oz. of impure purpurin, still containing madder-red, madder-yellow and alumina, are obtained. The product must therefore be washed with water, boiled with water containing hydrochloric acid, dissolved in alcohol of 90 p. c. and the solution evaporated until it begins to crystallise on the surface; the crystals thus obtained are again crystallised from alcohol and finally recrystallised from ether. (Runge.) Schiel, after washing the impure purpurin with water, dissolves it in a boiling solution of alum, filters the liquid from the deposit which is formed on cooling, and reprecipitates with sulphuric acid; he then continues the purification as above. Purpurin thus prepared still contains other colouring matters which remain in solution when the purpurin is dissolved in alcohol and treated with oxide of zinc, while a pure compound of purpurin and oxide of zinc is precipitated. (Debus.)

4. Zealand madder is boiled 3 or 4 times with 15 to 20 pts. of water, and the decoction is boiled with excess of hydrated oxide of lead, whereupon a part of the oxide of lead dissolves and the colouring matters are precipitated with the remainder, in the form of an insoluble compound. The well-washed precipitate is decomposed by warming with dilute sulphuric acid, and the resulting mixture of colouring matters with sulphate of lead is washed with water, and boiled with alcohol, which takes up the colouring matter, and leaves sulphate of lead together with a dark brown substance. The alcoholic solution is now shaken up with oxide of zinc, which is added in small portions as long as it continues to be coloured red; the whole is then boiled in order that the precipitate may settle down more readily; the resulting compound of the colouring matters with oxide of zinc is decomposed with dilute sulphuric acid; the liberated colouring matters are dissolved in ether, which leaves a brown resin; and the ethereal solution is again shaken with oxide of zinc, whereby the colouring matters are reprecipitated and fat remains in solution. When this zinc compound is again decomposed by dilute sulphuric acid, it deposits a mixture of alizarin and purpurin, which is washed and repeatedly boiled with a concentrated solution of alum. On cooling the decoctions, alizarin-alumina is deposited and purpurin remains dissolved; and on adding a little sulphuric acid to the solution, purpurin is slowly deposited and is obtained pure by boiling with dilute hydrochloric acid; washing with water, and recrystallisation from a large quantity of warm alcohol. (Debus.)

5. Oriental madder-root is cut up and immersed in boiling water, and to the reddish yellow extract acetate of lead is added, which precipitates all the purpurin and alizarin together with a little fat, citric acid, and traces of ruberythric, rubichloric, sulphuric, and phosphoric acids. The violet-coloured precipitate is washed with water and decomposed by sulphuretted hydrogen, and the liquid is separated from the precipitate of sulphide of lead, with which fat, alizarin and purpurin remain. The precipitate is then boiled with alcohol, and a dark brownish yellow solution of fat, purpurin and alizarin is thus obtained; and on adding water to this solution, it deposits gelatinous flakes of alizarin (containing a little fat and purpurin) which soon cohere, while purpurin remains dissolved. (Rochleder.)

*Properties.* Crystallises from strong alcohol in red anhydrous needles (Wolff and Strecker), several lines in length. (Gaultier and Persoz, Debus.) Light, mostly crystalline, orange-yellow powder. (Runge.) Solid mass like gamboge, of conchoidal fracture; its powder is of

beautiful rose-colour. (Gaultier & Persoz.) Brilliant, almost cherry-red powder. (Schiel.) Melts when heated (see *hydrated purpurin*) and sublimes (Colin & Robiquet) at  $225^\circ$  in beautiful cherry-red crystals, sometimes  $2\frac{1}{2}$  centim. in length (Schiel), leaving a residue chiefly of charcoal. (Gaultier & Persoz, Wolff & Strecker.) Melts, when carefully heated in a glass-tube, to a dark brown viscid liquid, giving off red vapours which condense not in needles, but as a red sublimate and a brownish red viscid mass. The sublimate retains unaltered the properties of purpurin, but cannot be resublimed without partial decomposition. (Runge.) According to Schiel, sublimed purpurin has a different composition and behaves differently with potash and solution of alum; this statement is not confirmed by Wolff & Strecker.

	At $120^\circ$ .			Debus. mean.
18 C .....	108	....	66.67	..... 66.40
6 H .....	6	....	3.70	..... 3.86
6 O .....	48	....	29.63	..... 29.74
$C^{18}H^6O^4$ .....	162	....	100.00	..... 100.00

Debus formerly gave the formula  $C^{15}H^5O^5$ . According to Rochleder, it is perhaps  $C^{60}H^{20}O^{20} = 3$  alizarin + 2Aq, which would explain the formation of similar products from alizarin and from purpurin. When purpurin is dried between  $115^\circ$  and  $120^\circ$ , it contains, on the average according to Schiel, 56.68 p. c. of C, and 3.48 p. c. of H, and corresponds to the formula  $C^{28}H^{10}O^{16}$ ; after sublimation, it contains 53.30 p. c. of carbon, and 5.19 p. c. of hydrogen, corresponding to the formula  $C^{28}H^{16}O^{16}$ . But according to Debus the purpurin which Schiel investigated was impure (see p. 326).

*Decompositions.* 1. Purpurin is less easily attacked by *nitric acid* than alizarin; after it has been completely dissolved and the excess of nitric acid has evaporated, oxalic and phthalic acids are obtained (p. 11).



Diluted nitric acid does not act on purpurin; concentrated acid produces a yellow liquid and oxalic acid. (Gaultier & Persoz.) — 2. It is more readily decomposed by *chlorine* than alizarin. (Gaultier & Persoz.)

*Combinations.* — *With Water.* — *a. Hydrate of Purpurin.* — Crystallises from weak alcohol in fine, soft, orange-yellow (reddish-yellow: Debus) needles, which give off at  $100^\circ$  about 4.86 per cent. of water (Wolff & Strecker); 4.9 p. c. water = 1 At. (calculation requires 5.2 p. c.) (Debus), and assume a red colour. (Wolff & Strecker). When heated, it melts to a reddish yellow liquid, which solidifies, on cooling, in long needles united concentrically and of the colour of red prussiate of potash. (Debus.)

*β. Aqueous Purpurin.* — Purpurin dissolves more readily in water than alizarin, imparting a wine-red (reddish, Wolff & Strecker) colour. (Colin & Robiquet.) It is scarcely soluble (Gaultier & Persoz, Schiel), sparingly (Runge, Debus) in cold water, more readily in boiling water (Schiel, Debus) with dark rose-colour, and is not separated from the solution on cooling. (Runge.) Dissolves more readily in water after being moistened with alcohol. (Schiel.) The aqueous solution is coloured yellow by acids. (Runge.)

When purpurin is boiled with dilute *acids*, it forms a yellow solution, from which it separates in orange-yellow flakes on cooling. (Runge.)

It dissolves in *oil of vitriol*, imparting to it a beautiful dark red colour, and may be precipitated by water unchanged. (Gaultier & Persoz.) A quantity of water equal to a quarter or one-third of the sulphuric acid solution precipitates the purpurin unchanged. Even when the solution is heated to 110°, the purpurin is not changed, but is again separated on slowly pouring the hot solution into cold water. (Schiel.) In the preparation of garancin, sulphuric acid should therefore be employed diluted with a quarter of its bulk of water (this strength of acid still chars the other substances) in order that no colouring matter may dissolve or be splashed away as fine powder on addition of water. (Schiel.) Purpurin dissolves unchanged even in hot *fuming sulphuric acid*, and is not decomposed till the temperature has reached 200°, when it blackens and evolves sulphurous acid. (Debus.)

Purpurin combines with bases and forms red or violet salts, which, with the exception of the potash, soda and ammonia compounds, are insoluble in water and in alcohol. (Debus.)

Dissolves in *ammonia* with magnificent deep red colour. (Runge.)

Dissolves in cold *sulphide of ammonium*; the dark red solution becomes still darker on standing with an excess of purpurin, and communicates a beautiful rose-coloured dye to stuffs. (Gaultier & Persoz.)

Dissolves readily in *alkalis*; and the solution which has a beautifully violet colour in the cold turns darker when warmed. (Gaultier & Persoz.) The solution of purpurin in alkalis is of a magnificent dark-red colour (Runge, Schiel), cherry-red or deep-red without blue reflection. (Wolff & Strecker.) According to Schiel, purpurin sublimed or strongly heated, forms a violet solution with potash; this was not confirmed by Wolff & Strecker. The solution loses its colour in the air, purpurin being precipitated (Gaultier & Persoz), (from absorption of carbonic acid, Gm.) Forms with acids a flocculent red precipitate (Schiel); is coloured yellowish red. (Gaultier & Persoz.) If the alkaline solution of purpurin containing alizarin is mixed with aqueous protosulphate of iron and allowed to stand in a stoppered bottle, a black precipitate is formed, together with a brownish yellow solution, which rapidly becomes blood-red in the air, and when mixed with hydrochloric acid deposits flakes of purpurin. (Rochleder.) Purpurin dissolves in the arsenites, arseniates, and silicates of the alkalis. (Gaultier & Persoz.)

Purpurin is insoluble in cold *alkaline carbonates* (Wolff & Strecker); it dissolves by heat, forming an archil-coloured solution, and separates again on cooling. (Gaultier & Persoz.)

The ammoniacal solution of purpurin gives a purple precipitate with baryta and lime-salts. (Wolff and Strecker.) Purpurin does not dissolve in *calcareous* spring-waters till all the lime together with a part of the purpurin has been precipitated in the form of a dark-red lake. (Runge.)

Dissolves readily in *alum* (with dark-red colour (Colin & Robiquet) and in *salts of alumina*, forming a beautiful cherry-red solution. (Gaultier & Persoz.) The cherry-red (bright-red, Wolff & Strecker) solution in boiling alum-liquor retains its colour after cooling and does not deposit any purpurin (a little, according to Wolff & Strecker), unless the latter was present in excess (Runge); but the purpurin is precipitated by sulphuric acid. (Wolff & Strecker.) Dissolves in aluminate of potash. (Gaultier & Persoz.)

Purpurin is insoluble in *stannous chloride*. It dissolves in all propor-

tions in stannous oxide mixed with a few drops of potash, forming a magnificent red solution which dyes fabrics red. (Gaultier & Persoz.)

*Compound of Purpurin.* — The ammoniacal solution of purpurin gives a purple precipitate with salts of lead. (Wolff & Strecker.)

When an alcoholic solution of acetate of lead is added in such quantity to an alcoholic solution of purpurin acidified with a little acetic acid, that an excess of purpurin remains, an abundant, beautiful violet precipitate is formed. The compound is stable at  $160^\circ$ , is insoluble in water, but dissolves in acetic acid and in potash. (Debus.) Its formula is  $C^{18}H^6O^4, PbO$ . (Debus.) It appears to be a mixture of neutral and basic lead-salt. (Wolff & Strecker.)

Calculation according to Wolff & Strecker.				Debus. at $120^\circ$ .
90 C .....	540	...	37.61	37.95
25 H .....	25	...	1.74	1.85
25 O .....	200	...	13.92	13.58
6 PbO .....	670.8	...	46.73	46.62
<hr/> 5( $C^{18}H^6O^4$ ), 6PbO .....				1435.8
				100.00
				100.00

Perhaps the formula is  $C^{60}H^{16}O^{16}, 4PbO$ . (Rochleder.)

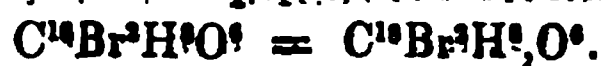
Purpurin dissolves in cold, and still more abundantly in hot *alcohol*. The solution is of much deeper red than that of alizarin. (Wolff & Strecker.) Purpurin also dissolves in absolute alcohol, forming an orange-yellow liquid which leaves a crystalline powder when evaporated. Addition of water causes the liquid to assume different colours, owing to the separation of needles having a silky lustre. (Runge.) The beautiful cherry-red solution turns violet-red when treated with potash, and after a time deposits purpurin. (Gaultier & Persoz.)

Purpurin dissolves very readily in ether, forming a still more brilliant red solution than with alcohol (Gaultier & Persoz); forming an orange-yellow solution. (Runge.)

Purpurin dyes fabrics mordanted with acetate of alumina, from deep red to purple-red and dark-brownish red, according to the quantity of purpurin employed; with zinc-mordant, it yields a rose-coloured dye; with acetate of lead, puce; and with iron-mordant, a violet-dye. It is incapable of forming Turkey-red. It dyes fabrics mordanted with copper-mordant reddish brown. (Runge.) Calico previously prepared with alum-mordant and gradually heated to boiling with an excess of purpurin, turns light brownish red, and when washed with soap, fine deep red. Calico prepared for Turkey-red with oil-mordant turns brownish red with purpurin, becoming fiery Turkey-red when washed with soap and carbonate of soda. (Wolff & Strecker.)

#### *Bromine-nucleus* $C^{18}Br^2H^8$ .

#### **Bibromophloretic Acid.**



HLASIWETZ. *Ann. Pharm.* 102, 161; *J. pr. Chem.* 72, 413.

Bromine is added by drops to powdered phloretic acid as long as any action takes place and hydrobromic acid is evolved; the mass, which is

at first doughy but afterwards hardens, is mixed well together; and the excess of bromine is allowed to evaporate; the remaining, slightly coloured powder is then repeatedly washed with water, dried over lime, and crystallised from alcohol. Colourless prisms are thus obtained, and in order to purify them completely, they are dissolved in warm dilute ammonia, precipitated with hydrochloric acid, and recrystallised from alcohol.

Hard, colourless prisms, melting very easily.

				Hlasiwetz.
18 C .....	108	...	33.33	33.49
2 Br.....	160	...	49.38	49.20
8 H .....	8	...	2.47	2.80
6 O .....	48	...	14.82	14.51
<hr/>				
$C^{18}Br^2H^8O^6$ ...	324	...	100.00	100.00

Insoluble in water.

*Bibromophloretate of Ammonia.*—When the acid is saturated with warm ammonia, the solution on cooling deposits short colourless needles. Cold alcoholic bibromophloretic acid becomes warm on adding ammonia and solidifies in a crystalline paste.

Gives off ammonia at a gentle heat. Dissolves slightly in cold water.

*Bibromophloretate of Baryta* separates in large quantities on mixing the ammonia-salt with chloride of barium.

Prisms, containing, when dried at  $120^{\circ}$ , 19.61 p. c. of baryta ( $C^{18}Br^2H^8O^6$ , BaO requires 19.49 p. c.)

Bibromophloretic acid dissolves readily in *alcohol*. The alcoholic solution evaporated in vacuo to the consistence of syrup, often fails to yield crystals, but when removed, soon solidifies in a hard crystalline paste.

Dissolves readily in *ether*.

*Nitro-nucleus*  $C^{18}X^2H^8$ ,

**Binitrophloretic Acid.**

$C^{18}N^2H^8O^{14} = C^{18}X^2H^8O^6$ .

HLASIWETZ. *Ann. Pharm.* 109, 155; *J. pr. Chem.* 72, 408.

*Preparation.* 1. Powdered phloretic acid is added to nitric acid of ordinary strength, the acid being kept cool, and each portion of the substance being allowed to dissolve before the next is added. The crystals formed after a short time are left to drain, then washed and recrystallised. — If nitric acid is poured upon phloretic acid, the acid dissolves at first with frothing, rise of temperature, and evolution of red vapours; but the solution on cooling becomes filled with yellow crystals of binitrophloretic acid. — 2. Nitric acid is added drop by drop to heated aqueous phloretic



acid, whereupon the liquid becomes coloured, effervesces and evolves hyponitric acid and then deposits yellow drops of resin. The latter is made to dissolve by continued heating and addition of a little nitric acid, after which the solution soon becomes filled with yellow crystals.

*Properties.* Prepared according to 1, it forms light lemon-yellow prisms; prepared according to 2: beautiful, very brilliant, laminæ and scales of a dark golden yellow colour. Tastes at first scarcely at all, then slightly bitter. Colours organic substances like picric acid. It does not lose weight at  $100^{\circ}$ .

					Hlasiwetz.			
					(1.)	(2.)		
18 C	.....	108	....	42·18	.....	41·92	....	42·65
2 N	.....	28	....	10·93	.....	10·95	....	10·91
8 H	.....	8	....	3·12	.....	3·46	....	3·37
14 O	.....	112	....	43·77	.....	43·67	....	43·07
<hr/>								
C <sup>18</sup> N <sup>2</sup> H <sup>8</sup> O <sup>14</sup>	.....	256	....	100·00	.....	100·00	....	100·00

*Decompositions.* 1. Melts, when heated on platinum, and burns with a smoky flame without explosion. — 2. Heated in a small tube, it yields a brown, oily distillate and yellow smoke. — 3. The ammoniacal solution of the acid treated with *sulphuretted hydrogen*, deposits sulphur. The dark red liquid leaves a residue on evaporation; and if this be dissolved in boiling water, filtered, and the solution mixed with hydrochloric acid, readily soluble crystals (probably hydrochlorate of biamidophloretic acid) are obtained.

*Combinations.* Dissolves very sparingly in cold water, forming a yellow solution. Dissolves readily in boiling water and crystallises rapidly on cooling.

Binitrophloretic acid is bibasic. Its normal salts are obtained by saturating the acid with carbonates or by double decomposition from binitrophloretate of ammonia. They explode when heated. The solutions of alkaline binitrophloretates have an intense yellowish-red colour. The ammonia-salt of the acid prepared according to 1 (designated below as acid  $\alpha$ ) gives crystalline precipitates with chloride of barium and chloride of calcium, which is not the case with the acid prepared according to 2 (acid  $\beta$  below). The neutral salts are, according to Hlasiwetz (*Ann. Pharm.* 102, 156), represented by the formula  $C^{18}H^7X^2M^2O^7$ , and according to another determination (*J. pr. Chem.* 72, 413) by  $C^{18}H^6X^2M^2O^6$ , the formula here adopted.

*Binitrophloretate of Ammonia.* — Effloresces in dark yellow needles when acid  $\beta$  supersaturated with ammonia is evaporated in vacuo.

					Hlasiwetz.	
18 C	.....	108	...	37.24		
4 N	.....	56	...	19.31	.....	18.29
14 H	.....	14	...	4.83	.....	5.04
14 O	.....	112	...	38.62		
<hr/>						
$C^{18}H^6X^2(NH^4)^2O^6$	.....	290	...	100.00		

According to Hlasiwetz's determination (*Ann. Pharm.* 102, 159), the salt contains an additional atom of water, which would require 18.72 p. c. N, and 5.01 p. c. H.

*Binitrophloretate of Potash.* — The salt prepared from acid crystallises on the spontaneous evaporation of its weak alcoholic solution, in dark orange-red prisms. The effloresced salt is of a deep red colour and appears green by reflected light. It dissolves more sparingly in dilute alcohol than in water.

At 120°.				Hlasiwetz.	
$C^{18}H^6X^2O^4$	.....	238	....	71.68	
2 KO	.....	94.4	....	28.32	..... 28.09
<hr/>					
$C^{18}H^6X^2K^2O^6$	.....	332.4	....	100.00	

*Binitrophloretate of Baryta.* — Acid  $\alpha$  or  $\beta$  is saturated with carbonate of baryta, or the solution of acid  $\alpha$  is neutralised with ammonia and precipitated with chloride of barium. Prepared from acid  $\alpha$ : orange-yellow needles which become deep red on standing; from acid  $\beta$ : orange-yellow, aggregated nodules, which turn red at 120°. The salt obtained from acid  $\alpha$  dissolves with difficulty in cold water.

At 120.				Hlasiwetz.	
				$\alpha$ .	$\beta$ .
$C^{18}H^6X^2O^4$	.....	238	....	60.86	
2 BaO	.....	153.2	....	39.14	..... 38.27 .... 38.36
<hr/>					
$C^{18}H^6X^2Ba^2O^6$	....	391.2	....	100.00	

$\alpha$  was prepared from acid  $\alpha$ ;  $\beta$  from  $\beta$ .

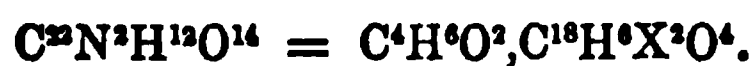
*Binitrophloretate of Lime.* — Obtained from acid  $\alpha$ , like the baryta-salt. Forms yellow needles.

Binitrophloretate of ammonia  $\alpha$  forms with acetate of zinc, a beautiful yellow amorphous precipitate; with *stannous chloride*, a yellowish precipitate, the solution becoming decolorised; with acetate of *lead*, a deep red precipitate; with *ferric chloride*, a light brown, flocculent precipitate; with *cupric salts*, a yellow precipitate; with *mercuric chloride* it produces a chrome-yellow, amorphous precipitate, which afterwards becomes crystalline and is soluble in an excess of mercurous chloride. Binitrophloretate of *silver*  $\alpha$  is red, and becomes crystalline on standing.

Binitrophloretate of ammonia  $\beta$  precipitates acetate of zinc and acetate of *lead* red, sulphate of *copper* yellow, and *mercuric chloride* reddish. The precipitates for the most part become crystalline on standing.

Binitrophloretic acid dissolves in *alcohol* and crystallises therefrom.

### Ethylbinitrophloretic Acid.



HLASIWETZ. *Ann. Pharm.* 102, 154; *J. pr. Chem.* 72, 406.

When phloretate of ethyl is treated with nitric acid, it is converted without violent action into a golden-yellow oil, which afterwards becomes



### 334 PRIMARY NUCLEUS $C^{15}H^{10}$ : OXYNITRO-NUCLEUS $C^{15}XH^5O^4$ .

solid and crystalline. This product is washed with water and recrystallised from alcohol.

Light-yellow, slightly bitter crystals which melt with facility.

					Hlasiwetz.
22 C .....	132	...	46.44	.....	46.76
2 N .....	28	...	9.87	.....	9.62
12 H .....	12	...	4.22		
14 O .....	112	...	39.47		
<hr/> $C^{15}H^{10}X^5O^4$ ....					284 .... 100.00

Dissolves very slightly in cold *water*, readily in *alcohol* and in *ether*.

#### Oxynitro-nucleus $C^{15}XH^5O^4$ .

#### Nitrocumarin.



DELALANDE. *N. Ann. Chim. Phys.* 6, 345; *J. pr. Chem.* 28, 256; *Ann. Pharm.* 45, 332.

BLEIBTREU. *Ann. Pharm.* 59, 190.

FRAPOLLI & CHIOZZA. *Ann. Pharm.* 95, 252; *J. pr. Chem.* 66, 342.

#### Nitrocumarine.

**Preparation.** When cumarin is added to cold fuming nitric acid, it dissolves almost immediately, with evolution of heat, and water precipitates snow-white flakes from the solution. (Delalande.) The liquid must not be allowed to boil, otherwise picric acid will be formed. (Bleibtreu.)

**Properties.** When crystallised from water, alcohol or ether, nitrocumarin forms small delicate needles having a silky lustre (Delalande) melting at  $170^{\circ}$ , and at a strong heat, subliming in white crystals of strong nacreous lustre. (Bleibtreu.)

					Delalande.	Bleibtreu.
18 C .....	108	...	56.54	.....	55.81	.... 56.02
N .....	14	...	7.34	.....	7.64	
5 H .....	5	...	2.62	.....	3.05	.... 2.64
8 O .....	64	...	33.50	.....	33.50	
<hr/> $C^{15}XH^5O^4$ .....					191 ....	100.00 ..... 100.00

**Decompositions.** 1. Nitrocumarin heated with *hydrate of potash* evolves ammonia, the yellowish red colour of the solution at the same time passing to blue. The residue dissolved in water and saturated with an acid, deposits a reddish brown powder. (Delalande.) — 2. Converted into cumarin by heating with dilute *acetic acid* and *iron filings*. (Frapolli & Chiozza.) It is not changed by nascent *hydrogen*, by *hypophosphite of potash* or *hypophosphite of ammonia*. (Frapolli & Chiozza.) When an

alcoholic solution of nitro-cumarin is saturated with gaseous ammonia, and the deep-red liquid thus obtained is saturated with sulphuretted hydrogen, sulphur is deposited; and on filtering and evaporating the solution, it yields a yellow viscid mass smelling of garlic which hardens in the air, and is insoluble in water, but moderately soluble in alcohol and in ether. (Bleibtreu.)

*Combinations.* Dissolves rather sparingly in boiling water, and crystallises out on cooling. (Bleibtreu.)

Dissolves in *ammonia*; the solution when boiled evolves ammonia and, on cooling, deposits part of the nitrocumarin out in white crystals which do not contain ammonia. (Bleibtreu.)

Dissolves in *alkalis*, forming a reddish yellow solution from which it is precipitated unchanged by acids. (Delalande, Bleibtreu.) It also remains unaltered when boiled for a long time with alcoholic potash. (Bleibtreu.)

*Lead-compound.* — The solution of nitrocumarin in ammonia, freed from excess of ammonia by boiling and filtered from precipitated nitrocumarin, gives with acetate of lead an orange-yellow precipitate, which is soluble in a large quantity of water, forming a yellow solution, still less soluble in alcohol and almost insoluble in ether; it is therefore purified by boiling with alcohol and ether. It is decomposed by acids, nitrocumarin being separated. (Bleibtreu.)

	At 100°.		Bleibtreu.
$C^{18}XH^5O^4$ .....	191	...	36.66
3 PbO .....	335.4	...	63.34
<hr/>			
$C^{18}XH^5O^4, 3PbO$ ....	526.4	...	100.00

*Silver-compound.* — Beautiful orange-coloured precipitate, obtained with nitrate of silver in the same manner as the lead-compound; behaves like the latter with water, acids, alcohol, and ether. Decomposes when dried in the water-bath. Explodes by heat. (Bleibtreu.)

	Dried in vacuo.		Bleibtreu.
$C^{18}XH^5O^4$ .....	191	...	45.17
2 AgO .....	232.2	...	54.83
<hr/>			
$C^{18}XH^5O^4, 2AgO$ .....	423.2	...	100.00

Nitrocumarin dissolves rather sparingly in boiling *alcohol* and in *ether*; on cooling it immediately crystallises in needles. (Bleibtreu.)

*Amidogen-nucleus*  $C^{18}AdH^6$ .

**Phloretylamic Acid.**

$C^{18}NH^{11}O^4 = C^{18}AdH^6, O^4$ .

HLASIWETZ. *Ann. Pharm.* 102, 162; *J. pr. Chem.* 72, 415.

Phloretate of ethyl (or the product of the action of iodide of ethyl upon phloretate of silver, which has not been distilled, but freed from

iodide of silver by filtration and from iodide of ethyl by heat) is left in contact with strong ammonia in a closed vessel, the whole being repeatedly shaken, till the ether has disappeared, and small crystals are deposited, for which several weeks are necessary. The ammonia and alcohol are then evaporated off, and the residue, which on cooling solidifies in a crystalline mass, is recrystallised from hot water.

Short, slender, brilliant prisms, melting between  $110$  and  $115^\circ$  and solidifying in a crystalline mass on cooling.

					Hlasiwetz.
18 C .....	108	....	65.46	.....	65.75
N .....	14	....	8.48	.....	8.05
11 H .....	11	....	6.66	.....	6.96
4 O .....	32	....	19.40	.....	19.24
<hr/>					
$C^{18}NH^{11}O^4$ ....	165	....	100.00	.....	100.00

Sublimes partly, when heated in a glass tube, and evolves large quantities of ammonia at a stronger heat.

Dissolves slightly in cold water. The solution colours sesquichloride of iron blue.

Dissolves in alcohol and in ether.

#### Azo-nucleus $C^{18}NH^9$ .

#### Cinchonidine.



WITTSTEIN. *N. Br. Arch.* 141, 32; *J. pr. Chem.* 72, 101.

*Source.* Found in the bark of *China pseudoregia*, a cinchona bark of unknown source, to the amount of  $3\frac{1}{2}$  per cent.

*Preparation.* The coarsely powdered bark is digested with warm water containing hydrochloric acid, and the strained reddish yellow liquid is allowed to stand for several days with an excess of milk of lime and then filtered. The precipitate is dried, powdered, and repeatedly treated with warm alcohol of 90 per cent.; it is then filtered, the greater part of the alcohol is distilled from the filtrate, and the residue is slowly evaporated. Almost colourless crystalline masses separate out, and are removed from the brown mother-liquor. The residue from the latter, after complete evaporation of the alcohol, is dissolved in water containing hydrochloric acid, and precipitated with ammonia. The precipitate is then redissolved in dilute hydrochloric acid, the solution is decolorised with animal charcoal and precipitated with ammonia; the precipitate is dissolved in alcohol; and the solution is gently evaporated to facilitate crystallisation.

*Properties.* Long, colourless, shining prisms. Melts between  $169^\circ$  and  $170^\circ$  C. Inodorous. Tastes bitter. Becomes electrical by friction. The alcohol has an alkaline reaction. Does not lose weight at  $160^\circ$ .

				Wittstein.
18 C .....	108	...	77.14	77.32
N .....	14	...	10.00	9.90
10 H .....	10	...	7.14	7.24
O .....	8	...	5.72	5.54
<hr/>				
$C^{18}NH^{10}O$ .....	140	...	100.00	.00

**Decompositions.** 1. Cinchonidine turns brown when heated and burns with a smoky flame. — 2. Dissolves readily and without coloration in fresh *chlorine water*, and is thrown down by ammonia as a greyish white precipitate; an excess of ammonia dissolves the precipitate, forming a wine-yellow solution. — 3. Yields, when distilled with *potash* of sp. gr. 1.33, a yellow oily base smelling of bitter almonds.

**Combinations.** Dissolves in about 3287 parts of cold and 596 parts of boiling *water*.

Dissolves unchanged in *oil of vitriol*, in concentrated *hydrochloric acid*, and in concentrated *nitric acid*, even on the application of gentle heat.

With hydrochlorate of cinchonidine, caustic alkalis and their carbonates produce a white precipitate; phosphate of soda, a white precipitate which afterwards becomes crystalline; iodide of potassium, a white crystalline precipitate; chloride of mercury, a white, flocculent precipitate; and terchloride of gold, a light lemon-yellow precipitate.

**Chloroplatinate of Cinchonidine.** — Precipitated in orange-yellow flakes on mixing hydrochlorate of cinchonidine with bichloride of platinum. The salt dried at  $110^{\circ}$  contains 28.5 p. c. of platinum (the formula,  $C^{18}H^{10}NO, HCl, PtCl^2$  requires 28.8 p. c.).

With hydrochlorate of cinchonidine, nitrate of palladium gives an orange-yellow flocculent precipitate; sulphocyanide of potassium, a white crystalline precipitate; and tannic acid a milk-white flocculent precipitate.

Cinchonidine dissolves in 88 pts. of cold, and in 19 pts. of boiling *alcohol* of sp. gr. 0.833. It dissolves in 398 pts. of cold *ether* of sp. gr. 0.74.

*Oxyazo-nucleus*  $C^{18}NH^5O^4$ .

**Cumaramine.**



A. FRAPOLLI & CHIOZZA. *Ann. Pharm.* 95, 252; *J. pr. Chem.* 66, 342.

**Formation and Preparation.** Nitrocumarin is added to a mixture of dilute acetic acid and iron filings, and the action, which quickly ensues, is promoted by warming the whole in a water-bath. A large quantity of ferric oxide separates out, and on cooling, yellow needles are deposited on the sides of the vessel. After 24 hours, the precipitate of ferric oxide is filtered from the ferrous acetate; the filtrate is evaporated; and the ferric oxide formed during the evaporation is separated by repeated filtration of the hot solution, which is then allowed to cool, whereupon yellow crystalline needles of cumaramine are deposited. The precipitated

ferric oxide also contains cumaramine, which is separated by treating the precipitate with alcohol, evaporating the alcoholic solution on the water-bath and redissolving the residue in water. The whole of the crystals are purified by repeated recrystallisation from water.

*Properties.* Beautiful, reddish-yellow needles of considerable length. Melts between  $168^{\circ}$  and  $170^{\circ}$ , and volatilises at a higher temperature in yellow vapours which condense to pale yellow laminæ, or distils when suddenly heated, as a heavy oil which solidifies on cooling.

Frapolli & Chiozza.					
18 C	.....	108	...	67.08	..... 67.4
N	.....	14	...	8.69	..... 9.1
7 H	.....	7	...	4.34	..... 4.4
4 O	.....	32	...	19.89	..... 19.1
<hr/>					
$C^{18}NH_7O^4$	.....	161	...	100.00	..... 100.0

*Decompositions.* 1. Cumaramine when suddenly heated, yields a small quantity of an oil smelling like aniline.

2. It is quickly decomposed by boiling potash-ley, acids then precipitating dark brown flocks.

*Combinations.* Cumaramine dissolves very sparingly in cold, easily in boiling water.

*Hydrochlorate of Cumaramine.* — Cumaramine unites readily with hydrochloric acid, forming a salt which crystallises in laminæ and dissolves easily in water; the solution mixed with ammonia solidifies into a crystalline magma of cumaramine.

*Chloroplatinate of Cumaramine.* — Bichloride of platinum added to a solution of hydrochlorate of cumaramine, produces a yellow crystalline precipitate insoluble in water.

Frapolli & Chiozza.					
$C^{16}NH^8O^4Cl^2$	.....	267.2	...	72.97	
Pt	.....	99.0	...	27.03	..... 26.7
<hr/>					
$C^{16}NH_7O^4, HCl, PtCl^2$	....	366.2	...	100.00	

Cumaramine dissolves in *ferrous acetate* more readily than in water. It dissolves in boiling *alcohol*, the saturated solution solidifying as it cools. It is nearly insoluble in *ether*.

### *Primary Nucleus $C^{18}H^{12}$ .*

#### *Cumol $C^{18}H^{12}$ .*

PELLETIER & WALTER. (1837.) *Ann. Chim. Phys.* 67, 299; *Pogg.* 44, 81; *Pharm. Centr.* 1857, 551.

GERHARDT & CAHOURS. (1840.) *N. Ann. Chim. Phys.* 1, 87, 372; *J. pr. Chem.* 23, 343; *Ann. Pharm.* 38, 88.

GERHARDT. *N. Ann. Chim. Phys.* 14, 107.

ABEL. *Ann. Pharm.* 63, 308; *Mém. Chem. Soc.* 8, 441; *Phil. Mag. J.* 32, 63.

CAHOURS. *Compt. rend.* 24, 557; 30, 321.

MANSFIELD. *Chem. Soc. Qu. J.* 1, 244; *Ann. Pharm.* 69, 179.

GERHARDT & LIÈS-BODART. *Compt. rend.* 29, 506; *Compt. chim.* 1849, 385; *Ann. Pharm.* 72, 293.

RITTHAUSEN. *J. pr. Chem.* 61, 79; *Pharm. Centr.* 1854, 350.

CHURCH. *Phil. Mag. J.* 9, 256; *J. pr. Chem.* 65, 383; *Pharm. Centr.* 1855, 400.

LIÈS-BODART. *Compt. rend.* 43, 394; *Pharm. Centr.* 1856, 797; *Ann. Pharm.* 100, 352.

WARREN DE LA RUE & H. MÜLLER. *Chem. Gaz.* 1856, 875; *J. pr. Chem.* 700, 30.

*Retinnyle* (Pelletier & Walter); *Cumène* (Gerhardt & Cahours); *Cume* (Gm.).

*Source.* In Burmese naphtha, that substance, when aqueous vapour at 200° is passed through it, yielding hydrocarbons, from which sulpho-cumolic acid is produced by the action of oil of vitriol. (Warren De la Rue & H. Müller.)

*Formation.* 1. In the distillation of cuminic acid with excess of baryta. (Gerhardt & Cahours.) — 2. In the dry distillation of the resin of *Pinus maritima* (Pelletier & Walter); of the wood, passing over into the crude spirit (Cahours); and of coal, being found in coal-tar naphtha (Mansfield, Ritthausen, Church.) — 3. In the distillation of phorone with anhydrous phosphoric acid. (Gerhardt & Liès; Liès.)

*Preparation.* 1. *From Cuminic Acid.* — 1 pt. of cuminic acid is gradually heated in a retort with 4 pts. of baryta. When the heat is carefully applied, and not more than 6 grammes of cuminic acid are used, nothing but colourless cumol passes over, while carbonate of baryta remains behind. The use of larger quantities at once is not to be recommended. (Gerhardt & Cahours.) Abel mixes cuminic acid with 4 pts. of lime and heats the mixture nearly to redness in a copper retort placed in a deep sand-bath. The colourless distillate has an unpleasant empyreumatic odour, which it retains even after rectification over hydrate of potash. Abel therefore distils it with concentrated chromic acid (which does not alter the cumol), distils (whereupon the bad smell is completely destroyed, and the pleasant odour of cumol becomes perceptible) and dries over chloride of calcium.

2. When the brown oil obtained in the preparation of illuminating gas by the dry distillation of the resin of *Pinus maritima*, is subjected to fractional distillation, toluol passes over between 130° and 160°, and then cumol. The latter is several times distilled, with separation of the first portion of the distillate, which contains toluol, then treated alternately with oil of vitriol and caustic potash, and each time distilled (the oil of vitriol removes naphthalin, but likewise destroys the cumol, if allowed to act too long), and finally rectified two or three times over potassium (whereby, however, the cumol is likewise attacked, with formation of carburet of potassium). (Pelletier & Walter.)

3. *From Light Coal-tar Naphtha.* — (Compare xi, 136.) Passes over between 140° and 145° (Mansfield); at 139° or 140°. (Ritthausen.) —

4. Passes over between  $145^{\circ}$  and  $148^{\circ}$ , in the rectification of the oil obtained from *wood-spirit* in the manner described at vol. xii. 175 (6). (Cahours.)

*Properties.* Colourless, strongly refracting oil. (Gerhardt & Cahours.) Transparent, colourless, less mobile than toluol. Sp. gr.  $0.87$  at  $43^{\circ}$ . (Pelletier & Walter.) Boils at  $144^{\circ}$  (Gerhardt & Cahours); at  $148^{\circ}$  (Abel, Cahours); at  $184.4^{\circ}$ , under an atmospheric pressure of  $0.76$  met. (Church); at  $150^{\circ}$  (Pelletier & Walter); at  $153^{\circ}$  (Gerhardt); and volatilises undecomposed. — Has a very agreeable odour, like that of benzol (Gerhardt & Cahours), but less pleasant (Ritthausen), like that of toluol. Its state is pungent and rather bitter. (Pelletier & Walter.)

					Pelletier & Walter. mean.	Gerhardt & Cahours. mean.
18 C .....	108	....	90	.....	89.48	.... 89.81
12 H .....	12	....	10	.....	10.08	.... 9.97
$C^{18}H^{12}$ .....	120	....	100	.....	99.56	.... 99.78

		Abel.	Gerhardt & Liès.	Liès.
18 C .....	90.34	...	...	98.57
12 H .....	9.88	...	10.2	10.28
<hr/>				
C <sup>18</sup> H <sup>12</sup> .....	100.22	...	...	99.85

	Vol.	Density.
C-vapour	18	7.4880
H-gas	12	0.8318
Cumol-vapour	2	8.3198
	1	4.1599

Pelletier & Walter examined cumol prepared from the resin of *Pinus maritima*; Gerhardt & Cahours and Abel, that from cuminic acid; Gerhardt and Liès that from phorone (p. 342, 1); and Liès that from phorone (p. 342, 2).

*Decompositions.* 1. Cumol is converted by fuming *sulphuric acid* into sulphocumolic acid. (Gerhardt & Cahours.) — 2. When *chlorine* is passed into boiling cumol, and the volatilised portion is cohobated, a thick faint-smelling oil is obtained, which burns slowly with a smoky green-edged flame; its vapour does not attack the eyes. (Pelletier & Walter.) — 3. By fuming *nitric acid*, it is converted into nitrocumol (Cahours, Nicholson), also by boiling with strong nitric acid, but by continued boiling it forms a peculiar acid. (Gerhardt & Cahours.) If the boiling be continued, the nitrocumol disappears again and is gradually converted into a yellowish crystalline mass, which dissolves in ammonia, with the exception of a small pulverulent residue. Hydrochloric acid added to the solution precipitates nitrobenzoic acid. (Abel, Cahours.) Dilute nitric acid converts cumol after four or five days' boiling, into benzoic acid. (Abel.) — Cumol is converted and turned yellow by nitric acid, even in the cold; on boiling, it dissolves, gives off a large quantity of nitrous acid gas

and a small quantity of hydrocyanic acid; with a sufficient quantity of nitric acid, a colourless solution is obtained, which deposits white flakes on cooling. These flakes, after washing with water, assume the appearance of a white unctuous matter, which dissolves sparingly in water, but easily in alkalis, forming a deep red solution from which acids precipitate red flakes. (Pelletier & Walter.)—4. A mixture of fuming *nitric* and fuming *sulphuric* acid converts cumol into binitrocumol. (Cahours.) The action takes place with difficulty and requires frequent renewal of the nitric acid to complete it. (Ritthausen.)—5. *Potassium* kept for some time in contact with cumol, blackens and becomes covered with a black crust, which appears to be carburet of potassium. (Pelletier & Walter.)—6. It is not altered by potash-ley or by hydrate of potash in the state of fusion. (Gerhardt & Cahours.)

*Combinations.* Cumol is insoluble in water. (Gerhardt & Cahours.)

With the aid of heat it dissolves *sulphur*, which crystallises out on cooling. It dissolves *iodine*. (Pelletier & Walter.)

It dissolves readily in *wood-spirit*, *alcohol*, *ether*, and *volatile oils*. (Gerhardt & Cahours.) It combines with *oils*, *fats*, and *most resins*. (Pelletier & Walter.)

**Mesitylene**  $C^{18}H^{12}$ , described at page 17, vol. ix, belongs properly to this place.

**Methol**  $C^{18}H^{12}$ , partly described at page 47, vol. ix. The following observations have since been made by Völckel. (*Ann. Pharm.* 86, 381.)

The light oils obtained in the distillation of wood, give off by rectification: between  $70^{\circ}$  and  $100^{\circ}$ , acetate of methyl and acetone; between  $100^{\circ}$  and  $150^{\circ}$ , toloul, xylol, and oxide of mesityl, together with a small quantity of methol; and from  $150^{\circ}$  to  $200^{\circ}$  oils free from oxygen, which when treated with sulphuric acid, as described at page 47, vol. ix, yield pure methol.

The methol thus obtained begins to boil at  $155^{\circ}$ , and distils over continuously as the boiling point rises to  $205^{\circ}$ . The distillate collected in five separate portions has a sp. gr. of 0.861 between  $150^{\circ}$  and  $160^{\circ}$  (a); 0.867 between  $160^{\circ}$  and  $170^{\circ}$  (b); 0.871 between  $170^{\circ}$  and  $180^{\circ}$  (c); 0.877 between  $180^{\circ}$  and  $190^{\circ}$  (d); 0.881 between  $190^{\circ}$  and  $265^{\circ}$  (e). It has a peculiar odour.

	a.		b.		c.		d.		e.
18 C .....	89.60	....	89.72	....	89.99	....	89.66	....	89.83
12 H .....	10.21	....	10.13	....	9.99	....	10.25	....	10.25
$C^{18}H^{12}$ .....	99.81	....	99.85	....	99.98	....	99.91	....	100.08

It is therefore (as well as that obtained according to ix, 47), a mixture of several volatile oils, isomeric with mesitylol and cumol. (Völckel.)

The hydrocarbon which was obtained by Cahours from crude wood-spirit, by treating it with oil of vitriol (xii, 228, 6), and distilled over between  $164^{\circ}$  and  $168^{\circ}$ , after the separation of the tuluol, xylol and cumol, perhaps also belongs to this place. According to Cahours (*Compt. rend.* 30, 321), it has the same composition and vapour-density as cumol and mesitylol, but is nevertheless different from both.

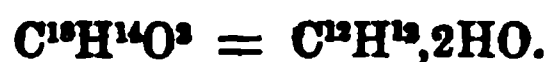
Methol burns with a smoky flame. It is decomposed after some time by strong nitric acid and by oil of vitriol.

It is insoluble in water, but dissolves readily in alcohol and ether.

Another hydrocarbon  $C^{18}H^{12}$ , isomeric with cumol, is obtained by distilling eugenic acid with excess of baryta. It boils at  $142^{\circ}$ . Forms a nitro-compound. (Church, *Phil. Mag.* [4], 9, 256.)



## Phorone.



LAURENT, (1837.) *Ann. Chim. Phys.* 65, 329.

GERHARDT & LIÈS-BODART. (1849.) *Compt. rend.* 29, 506; *Compt. chim.* 1849, 385; *Ann. Pharm.* 72, 293.

LIMPRICHT. *Ann. Pharm.* 94, 246.

LIÈS-BODART. *Compt. rend.* 43, 394; *Ann. Pharm.* 100, 352; *Pharm. Centr.* 1856, 797.

(*Camphoryle*. (Laurent.)

**Formation and Preparation.** 1. *From Camphorate of Lime.* — The salt is distilled in small portions, and the brown oil is rectified, a small quantity of tar then remaining. (Gerhardt & Liès.) Laurent obtained water, a brown oil, and a brown thick substance, with a residue of charcoal and carbonate of baryta. The oil dried with potash and distilled, yielded as the first half of the distillate, Laurent's camphoryl. — 2. *From Grape-sugar.* — When a thick syrup of grape-sugar is distilled with lime, an oil passes over, which at  $86^\circ$  begins to boil and yields metacetone, and afterwards at  $108^\circ$  yields phorone. (Liès.) — 3. *Metacetone* obtained according to (2), yields phorone by one distillation with anhydrous phosphoric acid. (Liès.) — 4. By the distillation of a syrupy substance contained in ripe *mountain-ash berries*. (Liès.) In a following year, mountain ash berries of the same degree of ripeness did not yield any phorone. (Liès.)

**Properties.** Colourless oil (Laurent); yellowish. (Gerhardt & Liès.) Very mobile. (Laurent.) Lighter than water. Boils at  $208^\circ$  (Gerhardt & Liès), between  $170^\circ$  and  $180^\circ$  (Laurent), and volatilises without decomposition. Has a strong odour, like that of peppermint. (Gerhardt & Liès.)

Vapour-density = 4.982. (Gerhardt & Liès.)

				Laurent.		Gerhardt & Liès.	
18 C	.....	108	....	78.26	.....	78.59	....
14 H	.....	14	....	10.15	.....	10.06	....
2 O	.....	16	....	11.59	.....	11.35	....
<hr/>				<hr/>		<hr/>	
$C^{18}H^{14}O^2$	.....	138	....	100.	.....	100.00	....
				Liès.			
				a.	b.	c.	
18 C	.....	108	.....	77.92	....	77.90	....
14 H	.....	14	.....	10.20	....	10.27	....
2 O	.....	16	.....	11.88	....	11.83	....
<hr/>				<hr/>		<hr/>	
$C^{18}H^{14}O^2$	.....	138	.....	100.00	....	100.00	....
				Vol.	Density.		
C-vapour	.....			18	.....	7.4880	
H-gas	.....			14	.....	0.9702	
O-gas	.....			1	.....	1.1093	
<hr/>				<hr/>			
Phorone-vapour	.....			2	.....	9.5675	
				1	.....	4.7838	

Laurent & Gerhardt and Liès examined phorone prepared by 1; that analysed by Liès (a) was prepared by 4, (b) by 2, and (c) by 3.

According to Laurent, phorone is  $C^{20}H^{14}O^2$ .

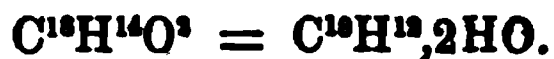
*Decompositions.* 1. Phorone becomes darker in colour when exposed to the *air*. (Gerhardt & Liès.)—It dissolves in *oil of vitriol*, forming a blood-red solution, from which the greater part of the oil is reprecipitated by water. (Gerhardt & Liès.)—3. It is rapidly attacked by *anhydrous phosphoric acid*, and by two distillations with that substance, it is converted into cumol. (Gerhardt & Liès, Liès.)—4. *Pentachloride of phosphorus* converts it into chloride of phoryl. (Liès.)—5. With *nitric acid* it gives off red vapours and is converted into a resin. (Gerhardt & Liès.)—6. Gently heated with *potassium*, it gives off hydrogen and appears to be converted into  $C^{18}H^{12}KO^2$ . (Liès.)—7. With *potash-lime* it becomes heated and appears to combine; and at  $240^\circ$  a colourless oil is given off which appears to be different from phorone. (Gerhardt & Liès.)

*Combinations.* Phorone is insoluble in water. It does not combine either with acids or with alkalis. (Laurent.)

It does not unite with alkaline bisulphites, either when it is shaken up with the aqueous solution of the potash or soda-salt, or when its alcoholic solution is mixed with an alcoholic solution of bisulphite of ammonia. (Limpricht.)

It dissolves in *alcohol* and with peculiar facility in ether. (Laurent.)

### Bihydrate of Mesitylene.



LIMPRICHT, *Gött. Nachrichten* 1858, 246.

When acetone is left for several weeks in contact with burnt marble, and the resulting mass is distilled, acetone passes over first, then at  $129^\circ$  the compound  $C^{12}H^{10}O^2$ , and lastly at  $210^\circ$ , bihydrate of mesitylene. The latter is  $C^{18}H^{14}O^2 = 3C^6H^4O^2 - 4HO$ . It boils between  $210^\circ$  and  $220^\circ$ , but turns brown and decomposes to a certain extent.

It is isomeric or perhaps identical with phorone. (Kr.)

### Chloride of Phoryl.



LIÈS-BODART. *Compt. rend.* 43, 394; *Ann. Pharm.* 100, 353.

Obtained by treating phorone with pentachloride of phosphorus.

Oil, having an agreeable odour and boiling at about  $175^\circ$ . Lighter than water.

				Lièz-Bodart.	
18 C	.....	108	....	69.04	..... 68.83
Cl	.....	34.5	....	22.66	..... 23.10
13 H	.....	13	....	8.30	..... 8.07
<hr/>					
$C^{18}ClH^{13}$	.....	156.5	....	100.00	..... 100.00

Decomposes when its alcoholic solution saturated with gaseous ammonia is heated in a sealed tube, yielding a few crystals which contain an amount of chlorine corresponding to the formula  $C^{18}H^8N, HCl$ .

### Sulphocumolic Acid.



GERHARDT & CAHOURS. *N. Ann. Chim. Phys.* 1, 90.

*Cumeschwefelsäure, Acide sulfocuménique.*

Known only in combination with water and baryta.

*Formation.* By bringing cumol in contact with fuming oil of vitriol.

*Preparation of the Baryta-salt.* — 2 pts. of fuming oil of vitriol are poured upon 1 pt. of cumol in a glass cylinder, and the liquid is stirred with a glass rod till the whole of the cumol is dissolved. When large quantities are used, the whole may be left to stand in a closed vessel, the cumol then dissolving gradually. The dark brown solution is diluted with 4 volumes of water, whereupon, if the cumol and the acid have been long enough in contact, a colourless solution is formed, without separation of cumol; and the liquid is saturated with pulverised carbonate of baryta, then filtered and evaporated: on cooling, it yields sulphocumolate of baryta. The colourless mother-liquor yields, to the last drop, the same salt, which may be obtained pure by pressure between paper.

*Sulphocumolate of Baryta* forms very beautiful scales, having a strong pearly lustre. It dissolves very easily in water, especially when hot. It is soluble in alcohol, even in anhydrous alcohol, and likewise in ether.

				Gerhardt & Cahours.	
				<i>mean.</i>	
<i>At 100°.</i>					
Ba	.....	68.5	....	25.61	..... 25.73
18 C	.....	108	....	40.34	..... 39.94
11 H	.....	11	....	4.11	..... 4.32
2 S	.....	32	....	11.96	..... 11.59
6 O	.....	48	....	17.98	..... 18.42
<hr/>					
$C^{18}H^{11}Ba, 2SO^3$	....	267.5	....	100.00	..... 100.00

A specimen prepared with cumol obtained from phorone, contained 25.2 p. c. barium. (Gerhardt & Lièz.)

Sulphocumolate of baryta does not precipitate chloride of calcium, neutral acetate of lead, or the chlorides of bismuth, nickel, copper or mercury.

Gerhardt & Cahours, on treating the cumol obtained by Pelletier & Walter (p. 339, 2) with fuming sulphuric acid, found that it dissolved slowly but completely, forming a brown-red solution. This liquid diluted with water and thereby rendered colourless, yielded, when saturated with carbonate of baryta, a baryta-salt less soluble in water than sulphocumolate of baryta, so that the strongly concentrated solution did not solidify on cooling, but gradually yielded on its surface crystalline crusts destitute of pearly lustre. From the residue left on evaporating the solution to dryness, ether extracted a resin, but not completely: for the salt still crystallised badly, even from a solution in water containing alcohol. It dissolved with difficulty in absolute alcohol.

	At 100°.		Gerhardt & Cahours.
Ba .....	68.5	....	25.61
18 C .....	108	....	40.34
11 H .....	11	....	4.11
2 S .....	32	....	11.96
6 O .....	48	....	17.98
<hr/>			
$C^{18}H^{11}Ba, 2SO^3$ .....	267.5	....	100.00
			..... 100.00

Sulphomesitylic or Sulphomesitylosulphuric Acid  $C^{18}H^{12}, 2SO$  [see vol. ix, p. 30.]

*Oxygen-nucleus*  $C^{18}H^6O^6$ .

**Bergaptene**  $C^{18}H^6O^6$ ?

KALBRUNER. *Baumgärt. Jahrb. Phys.* 3, 367.

MULDER. *J. pr. Chem.* 17, 104; *Ann. Pharm.* 31, 70.

OHME. *Ann. Pharm.* 31, 320; *N. Br. Arch.* 53, 287.

*Hydrate of Bergamot-oil, Stearoptene of Bergamot-oil, Bergamot-camphor.*

*Source.* In oil of bergamot, being the chief constituent of the sediment which forms on keeping. (Ohme.)

*Purification.* The sediment is pressed between bibulous paper frequently renewed; then dried at 100° (whereupon it loses half its weight, acquires a dirty yellow colour, and becomes friable), washed with cold alcohol to remove resin, and dissolved in boiling alcohol. The solution evaporated to one-third of its bulk, deposits crystals, of which the mother-liquor does not yield any more. (Kalbruner.) Mulder leaves the sediment to crystallise from alcohol. Ohme presses and treats it with ether, to dissolve the oil, and then crystallises repeatedly from hot alcohol.

*Properties.* Short white needles having a silky lustre, and melting at a high temperature (at 206.5° according to Mulder) to a colourless oil, which solidifies in the crystalline form on cooling. (Kalbruner, Ohme.) Inodorous. Tasteless. Neutral. Volatile without decomposition (p. 346).

				Mulder.		Ohme.
18 C	.....	108	.....	66·67	... 67·02	... 67·21
6 H	.....	6	.....	3·70	... 3·88	... 3·80
6 O	.....	48	.....	29·63	... 29·10	... 28·99
<hr/>						
$C^{18}H^6O^6$	.....	162	.....	100·00	... 100·00	... 100·00

*Decompositions.* 1. Melts over the flame of a spirit-lamp to a yellow oil, then turns black, volatilises for the most part in dazzling white flakes soluble in oil of vitriol and in alcohol, and leaves charcoal. (Kalbruner.) The vapour decomposes at a few degrees above the melting point. (Mulder.) — 2. Burns with a bright flame when set on fire. — 3. Coloured red by oil of vitriol. — 4. Decomposed by hot, but not by cold *nitric acid*, without formation of oxalic acid. (Mulder.) — 5. Does not absorb either *hydrochloric acid* or *ammonia-gas*. (Kalbruner.)

*Combinations.* Bergaptene is nearly insoluble in water. (Ohme.) It dissolves in 2000 parts of boiling water, and separates on cooling in flakes; from a solution four times diluted it separates on cooling in beautiful capillary crystals. (Kalbruner.) The solution does not precipitate lime-water, chloride of barium, ferrous sulphate, nitrate of silver, oxalic acid or tincture of galls. (Kalbruner.)

It is insoluble in dilute sulphuric acid but dissolves in oil of vitriol, and is precipitated from the solution by water, but not by alcohol. (Kalbruner.) It does not dissolve in *hydrochloric acid* (Kalbruner, Mulder), or in *ammonia* (Mulder); partially in ammonia on boiling. (Kalbruner.)

It dissolves in cold strong *nitric acid*, and is precipitated by water. (Kalbruner.)

It dissolves in *potash-ley*, forming a red-brown liquid, whence it is separated as a white precipitate by acids, but not by water or alcohol. (Kalbruner.)

It dissolves at 15° in 200 parts of *alcohol* of sp. gr. 0·85 (Kalbruner), abundantly in boiling alcohol, — so that the solution forms a solid mass on cooling. (Ohme.) Soluble in *ether*. (Mulder.) Dissolves in warm *acetic acid*, whence it is precipitated by water. Insoluble in dilute *acetic acid*. (Kalbruner.)

Terbromomesitylene  $C^{18}Br^3H^9$  (ix, 19).

#### Chlorine-nucleus $C^{18}Cl^3H^{10}$ .

#### Oil from Thymol $C^{18}Cl^3H^{10}$ .

LALLEMAND. *Compt. rend.* 43, 375; *Ann. Pharm.* 101, 125; *N. Ann. Chim. Phys.* 49, 148; *Ann. Pharm.* 102, 124.

When 30 or 40 grammes of thymol contained in a retort is treated with excess of chlorine, a viscid product is formed, which, on exposure to the sun, and afterwards on distillation, gives off propylene-gas ( $C^3H^6$ ), and yields a distillate of solid terchlorotoluenol ( $C^{14}H^6Cl^3O^2$ ) which boils at 270°, and a liquid boiling at 365°. This liquid contains  $C^{18}Cl^3H^{10}$  and is probably therefore bichloride of cumol.

*Nitro-nucleus*  $C^{18}XH^{11}$ .

### Nitrocumol.



CAHOURS. *Compt. rend.* 24, 552; 26, 315.

NICHOLSON. *Ann. Pharm.* 65, 58; *Chem. Soc. Qu. J.* 1, 2.

RITTHAUSEN. *J. pr. Chem.* 61, 79; *Pharm. Centr.* 1854, 350.

*Nitrocume, Cumène nitrique, Nitrocume.*

*Formation.* From cumol and fuming nitric acid (p. 340).

*Preparation.* Cumol is dissolved in fuming nitric acid, whereupon the mixture becomes hot and gives off abundance of red vapours, and the nitrocumol is precipitated as a heavy oil on the addition of water. (Nicholson.)

*Properties.* Yellowish oil, having a fainter and less agreeable odour than nitrobenzol. (Ritthausen.)

By *sulphuretted hydrogen* in presence of alcohol and ammonia, it is converted into cumidine. (Cahours, Nicholson.)

**Nitromesitylene**  $C^{18}XH^{11}$  (ix, 20).

*Nitro-nucleus*  $C^{18}X^2H^{10}$ .

### Binitrocumol.



CAHOURS. *Compt. rend.* 24, 552; 26, 315.

RITTHAUSEN. *J. pr. Chem.* 61, 79.

*Binitrocume, Cumène binitrique.*

*Formation and Preparation* (p. 346)

Crystallises from alcohol in white laminæ. (Ritthausen.)

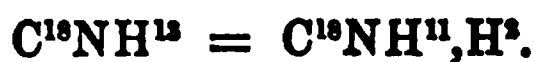
*Hydrosulphate of Ammonia* readily converts it into nitrocumidine. (Cahours.) It is insoluble in caustic alkaline-leys, but dissolves in alcoholic potash, and is converted thereby into nitrotoluol. Hydrochloric acid precipitates brown flakes from the solution. (Ritthausen.)

**Binitromesitylene**  $C^{18}X^2H^{10}$  (ix, 20).

**Ternitromesitylene**  $C^{18}X^3H^9$  (ix, 21).

*Azo-nucleus*  $C^{18}NH^{11}$ .

### Cumidine.



CAHOURS. (1847.) *Compt. rend.* 24, 557; 26, 315; 30, 321.

ED. CHAMBERS NICHOLSON. *Ann. Pharm.* 65, 58; *Chem. Soc. Qu. J.* 1, 2.

A. W. HOFMANN. *Ann. Pharm.* 66, 145; 74, 15.

RITTHAUSEN. *J. pr. Chem.* 61, 79; *Pharm. Centr.* 1854, 350.

CHURCH. *Phil. Mag.* [3] 9, 454.

*Cumidin, Cumine.*

Discovered by Cahours, investigated by Nicholson.

*Formation* (p. 347.)

*Preparation.* Nitrocumol is dissolved in alcohol and the solution is saturated, first with ammonia, then with sulphuretted hydrogen. After a few days, when a large quantity of sulphur has been deposited and the odour of sulphuretted hydrogen is no longer perceptible, sulphuretted hydrogen is again passed through the solution and the liquid is distilled, whereby the decomposition of the sulphuretted hydrogen is accelerated; and this treatment is repeated till the whole of the nitrocumol has disappeared. The alcohol and hydrosulphate of ammonia are then removed by distillation; the residue is dissolved in hydrochloric acid; the liquid filtered from the sulphur is evaporated till it solidifies in a crystalline mass on cooling; and the boiling solution of hydrochlorate of cumidine is treated with potash to separate the base, which rises to the top of the liquid as an oily layer. This oil is rectified and supersaturated with a concentrated solution of oxalic acid; the liquid is evaporated to dryness; the residue dissolved in boiling alcohol; and the solution treated with blood-charcoal: the filtrate, on cooling deposits perfectly pure colourless prisms of oxalate of cumidine. This salt is dissolved in water; the solution decomposed by potash; and the layer of oil which rises to the surface, is removed with a pipette, dried over chloride of calcium, and rectified. (Nicholson.)

*Properties.* Pale yellow, or when recently distilled, nearly colourless oil, of sp. gr. 0.9526. Refracts and disperses light strongly. When cooled by a mixture of ice and salt, it solidifies in a mass of square plates, which quickly melt again as the temperature rises. (Nicholson once obtained these plates in winter without the use of a freezing mixture, and then they remained solid.) Dropped upon paper, it forms a grease-spot which gradually disappears. In contact with platinum-wire, it boils constantly at  $225^{\circ}$ , when the barometer stands at 0.761 met. Has a peculiar odour and burning taste. Neutral to turmeric and red litmus paper. Colours pine-wood intensely yellow (like aniline and toluidine) but does not exhibit the reaction of aniline with chloride of lime. (Nicholson.)

				Nicholson.
18 C .....	108	....	80.00	..... 79.82
N .....	14	....	10.37	..... 10.67
13 H .....	13	....	9.63	..... 9.66
<hr/>				
$C^{18}NH^{13}$ .....	135	....	100.00	..... 100.15

*Decompositions.* 1. Cumidine exposed to the *air*, even for a few minutes only, turns yellow and then dark red, especially if warmed. — 2. The vapour burns with a yellow, very fuliginous flame. — 3. It is violently attacked by *chlorate of potash* and *hydrochloric acid* and converted into a brown viscid mass, which smells strongly like terchlorocarbonic acid, and is dissolved by alcohol, leaving a residue of chloranil. — 4. By *bromine* it is converted, with rise of temperature and evolution of hydrobromic acid, into a solid mass which is insoluble in water, but soluble in alcohol and ether, crystallises in white needles, and is perhaps terbromocumidine ( $C^{18}NH^{10}Br^3$ ). — 5. Strong *nitric acid* dissolves cumidine with splendid purple colour, and water added to the liquid throws down flakes which appear to be an acid. — 6. Dry *chromic acid* becomes very hot in contact with cumidine, but does not set it on fire. — 7. In phosgene-gas, cumidine is immediately converted into a crystalline mass, which separates from alcohol in long crystals like nitre: probably carbocumidine,  $C^{18}NH^{12},CO$ . — 8. Cumidine dissolves in bisulphide of carbon, and then gives off a large quantity of sulphuretted hydrogen; water added to the solution, throws down after a long time, a quickly solidifying oil, which crystallises from alcohol in long needles: probably sulphocarbocumidine,  $C^{18}NH^{12},CS$ , corresponding to the aniline-compound. (Nicholson.) — 9. When dissolved in water, it is converted by *cyanogen gas* into cyanocumidine. (Hofmann.) — 10. With *anilocyanic acid*, it immediately solidifies to a solid crystalline mass, probably carbanilide-carbocumidine:  $C^{14}H^5NO^2 + C^{18}NH^{12} = C^{32}N^2H^{18}O^2$ . (Hofmann.)

*Combinations.* Cumidine dissolves very sparingly in *water*; very easily in *bisulphide of carbon*.

*With Acids.* — Cumidine is a very weak base. It precipitates sesquioxide of iron from ferric salts. It does not precipitate alumina or zinc-salts. Its salts crystallise very easily, and, with the exception of a few double salts containing chlorides of the heavy metals, are colourless, but turn reddish on exposure to the air, or when dried at a very high temperature. They have an acid reaction and are anhydrous, like the salts of aniline. From concentrated solutions of cumidine-salts, alkalis separate the cumidine in dark oil-drops, and from dilute solutions in the form of a curd. All the salts of cumidine dissolve in water, but better in alcohol. (Nicholson.)

*Phosphate of Cumidine* crystallises readily.

*Sulphate of Cumidine.* — When cumidine is dissolved in boiling dilute sulphuric acid, the solution solidifies on cooling, in a crystalline mass, which may be obtained perfectly pure by recrystallising with animal charcoal.

Inodorous; has an unpleasantly bitter taste. At  $100^\circ$  it gives off



the odour of cumidine, and assumes a reddish colour, without further alteration. Dissolves sparingly in cold water, much more readily in alcohol.

					Nicholson.
18 C	.....	108	...	58.70	..... 58.66
N	.....	14	...	7.61	
14 H	.....	14	...	7.60	..... 7.94
O	.....	8	...	4.35	
SO <sup>3</sup>	.....	40	...	21.74	..... 21.77
<hr/>					
$C^{18}NH^{12}, HO, SO^3$	...	184	...	100.00	

*Hydriodate of Cumidine* crystallises readily: it appears to be the most soluble of the cumidine-salts.

*Hydrobromate of Cumidine* crystallises readily.

*Hydrochlorate of Cumidine.* — The combination of cumidine with hydrochloric acid is attended with evolution of heat. The salt crystallises from water and alcohol in large, colourless, inodorous prisms which turn red in the air when moist. It does not undergo any alteration at 100°, but melts and sublimes when strongly heated.

					Nicholson.
18 C	.....	108	...	62.97	..... 62.94
N	.....	14	...	8.17	
14 H	.....	14	...	8.17	..... 8.34
Cl	.....	35.5	...	20.69	..... 20.67
<hr/>					
$C^{18}NH^{12}, HCl$	...	171.5	...	100.00	

*Hydrofluorate of Cumidine* crystallises.

*Nitrate of Cumidine.* — When cumidine is dissolved in dilute nitric acid, the liquid becomes filled, on cooling, with long needles, which are colourless, if the acid used was not too strong. The salt remains unaltered at 100°. It is soluble in water and in alcohol.

					Nicholson.
18 C	.....	108	...	54.54	..... 54.52
2 N	.....	28	...	14.15	
14 H	.....	14	...	7.07	..... 7.37
6 O	.....	48	...	24.24	
<hr/>					
$C^{18}NH^{12}, HO, NO^3$	...	198	...	100.00	

Sulphate of copper forms with alcoholic cumidine, a precipitate of a fine green colour.

*Protochloride and Cyanide of Mercury*, form with alcoholic cumidine, white crystalline precipitates which are decomposed by boiling water.

With *Terchloride of Gold*, alcoholic cumidine forms a violet precipitate which dissolves with violet colour in a larger quantity of alcohol.

*Chloroplatinate of Cumidine.* — When a warm aqueous solution of

hydrochlorate of cumidine is mixed with excess of bichloride of platinum, the liquid on cooling, deposits long yellow needles, which may be obtained pure by washing with cold water.

The salt becomes darker at 100°, without further alteration, and at a stronger heat, gives off hydrochlorate of cumidine, and leaves a residue of platinum. It is decomposed by boiling water. Alcohol dissolves it in large quantity, and the solution yields after a while, dark red oil-drops, which, after the alcohol has evaporated, solidify in a crystalline mass of splendid orange-yellow colour.

				Nicholson.	Church.
18 C	.....	108	....	31.65	..... 31.38
N	.....	14	....	4.12	
14 H	.....	14	....	4.12	..... 4.48
Pt	.....	98.7	....	28.90	..... 28.89 .... 28.89
3 Cl	.....	106.5	....	31.21	
<hr/>					
$C^{18}NH^{13}, HCl, PtCl^2$	.....	341.2	....	100.00	

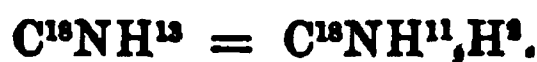
With *Bichloride of Palladium*, hydrochlorate of cumidine forms a double salt, resembling the platinum-salt in appearance.

*Acetate of Cumidine* crystallises readily.

*Oxalate of Cumidine.* — Cumidine forms with oxalic acid a neutral and an acid salt, which are both crystallisable but cannot be separated; when subjected to dry distillation, they yield a slightly crystalline mass, which dissolves sparingly in alcohol and exhibits the relations of oxycumidine. (Nicholson.)

Cumidine dissolves very easily in *wood-spirit, alcohol, ether, and fatty-oils.* (Nicholson.)

### Parvoline.



C. GREVILLE WILLIAMS. *Chem. Soc. Qu. J.* 7, 97; *J. pr. Chem.* 62, 467; *N. Ann. Chim. Phys.* 45, 493.

*Source.* In naphtha from Dorsetshire shale. (p. 148.)

The portion, boiling above 200°, of the bases obtained by the process described at page 148, 3 of this volume, is collected apart.

				Gr. Williams.
18 C	.....	108	....	80.00
N	.....	14	....	10.37
13 H	.....	13	....	9.63
<hr/>				
$C^{18}NH^{13}$	.....	135	....	100.00

Isomeric with Cumidine. Homologous with collidine.

*Oxyazo-nucleus*  $C^{10}N^2H^6O^4$ .**Acid from Naphthylamine.**

GANAHL & CHIOZZA. *Ann. Pharm.* 99, 240; *J. pr. Chem.* 70, 125.

*Formation.* By the action of nitrous acid on naphthylamine or nitrate of naphthylamine.

*Preparation.* Nitric acid gas is passed into naphthylamine moistened with water (nitrogen being thereby evolved) till the mass acquires a yellowish brown colour; the whole is heated to the boiling point, and left to itself till the brisk evolution of gas, which continues several hours after cooling, has ceased; the resulting brown powder is collected on a filter, washed with water and dissolved in boiling alcohol, and water is added to the solution as long as orange-yellow flakes continue to fall down; these may be repeatedly crystallised from alcohol.

*Properties.* Reddish brown needles, consisting of microscopic, transparent, yellow laminæ. Colours the skin and the tissues yellow. Sublimes without detonating.

						Ganahl.
18 C	.....	108	...	52.4	.....	52.80
2 N	.....	28	...	13.6	.....	12.50
6 H	.....	6	...	2.9	.....	3.26
8 O	.....	64	...	31.0	.....	31.44
<hr/>						
$C^{10}N^2H^6O^8$	.....	206	...	100.0	.....	100.00

With *ammonia*, when the solution is left to evaporate, it forms a salt which crystallises in yellow laminæ and dissolves easily in boiling water. The ammonia salt forms a lemon-yellow precipitate with potash and soda and orange-yellow with baryta and lead salt. With nitrate of silver it forms an orange-yellow precipitate containing 33.33 per cent. of silver ( $C^{10}N^2H^6AgO^8 = 34.50$  Ag.)

The acid is soluble in *ether*.

*Nitroazo-nucleus*  $C^{10}NXH^{10}$ .**Nitrocumidine.**

CAHOURS. *Compt. rend.* 24, 557; 26, 315.

*Nitrocumine.*

*Formation and Preparation.* Binitrocumol dissolved in alcohol is treated with hydrosulphate of ammonia, complete decomposition quickly ensuing.

*Properties.* Yellow crystalline scales which melt below  $100^{\circ}$ , and solidify in a radiating mass on cooling. The compound exerts a slight but distinct alkaline reaction on test-paper.

				Calours.	
18 C .....	108	....	60.00	.....	59.79
2 N .....	28	....	15.56	.....	15.71
12 H .....	12	....	6.67	.....	6.63
4 O .....	32	....	17.77	.....	17.87
<hr/>					
$C^{18}N^2H^{12}O^4$ ....	180	....	100.00	.....	100.00

*Decompositions.* 1. Partially decomposed by distillation; nevertheless the greater part passes over unaltered. — 2. *Bromine* acts violently upon it, converting it into a crystalline product which is no longer basic. — 3. It is not altered by *chloride of benzoyl* at ordinary temperatures, but between  $50^{\circ}$  and  $60^{\circ}$  it is converted, with violent action, into a crystalline product, which when dissolved in alcohol, after being washed with acid, alkaline, and pure water, crystallises in snow-white needles, containing  $C^{32}N^2H^{16}O^6 = C^{14}H^6O^2, C^{18}N^2H^{12}O^4$ , corresponding therefore to benzamide and benzanilide. — 4. With *chloride of cumyl* and *chloride of cinnamyl*, it forms products similar to that with chloride of benzoyl.

*Combinations.* Nitrocumidine is insoluble in water. It neutralises acids completely, even the strongest, forming salts which crystallise well. These salts, if exposed to air in the moist state or in solution, decompose quickly, assuming a greenish blue colour.

*Sulphate of Nitrocumidine.* — Obtained by dissolving nitrocumidine in hot dilute sulphuric acid, and leaving the solution to cool slowly. Long needles having a strong lustre. May be pulverised. Contains  $C^{18}N^2H^{12}O^4, SO^1 + 2Aq$ .

*Hydrochlorate of Nitrocumidine.* — The saturated solution yields by slow cooling, white silky needles, which in the dry state, are composed of  $C^{18}N^2H^{12}O^4, HCl. + 2Aq$ .

*Oxalate of Nitrocumidine.* — Slender needles.  
Nitrocumidine dissolves readily in *alcohol* and in *ether*.

Nitromesidine  $C^{18}N^2H^{12}O^4 = C^{18}NXH^{10}H^2$  [ix, 21].

*Conjugated compound containing a nucleus derived from 2 At.  $C^{18}NH^{11}$ .*

### Cyanocumidine.



A. W. HOFMANN. (1848.) *Ann. Pharm.* 66, 145.

*Formation* (p. 349).

The alcoholic solution of cumidine, saturated with cyanogen gas, quickly deposits long needles, which are easily purified by recrystallisation from alcohol.

						Hofmann.
40 C	.....	240	....	74.53	.....	74.33
4 N	.....	56	....	17.40		
26 H	.....	26	....	8.07	.....	8.32
<hr/>						
$C^{40}N^4H^{26}$	.....	322	....	100.00		

Hofmann adopts the simple formula  $C^{20}N^2H^{13}$ , but according to page 359, vol. xi, this formula ought to be doubled.

Cyanocnmidine forms with *hydrochloric acid* a salt nearly insoluble in water.

It dissolves in *alcohol* more readily than cyananiline.

*Primary Nucleus*  $C^{18}H^{14}$ .

*Oxygen-nucleus*  $C^{18}H^{14}O^4$ .

**Veratric Acid.**

$C^{18}H^{10}O^8 = C^{18}H^{10}O^4, O^4$ .

C. MERCK. (1839.) *Ann. Pharm.* 29, 188.

A. SCHRÖTTER. *Ann. Pharm.* 29, 190.

W. MERCK. *Compt. rend.* 47, 36.

Discovered by C. Merck in *sabadilla* seed.

*Preparation.* Sabadilla seeds are exhausted with alcohol containing sulphuric acid; the filtered tincture is mixed with hydrate of potash and again filtered; the alcohol distilled off; the separated veratrin collected; and the mother-liquor supersaturated with sulphuric acid: the acid then crystallises, either after standing for a few hours, or at all events after the liquid has been evaporated to one-half its bulk and filtered from the gypsum. The acid is washed with cold water and dissolved in boiling alcohol, and the solution is digested with animal charcoal free from lime, then filtered and left to crystallise. (C. Merck.)

*Properties.* Colourless needles and four-sided prisms. Reddens litmus-paper. When heated, it gives off water, becomes dull, melts to a colourless liquid and volatilizes without decomposition. Heated in a glass tube, it yields a crystalline sublimate and vapours which redden litmus. (C. Merck.)

						Schrötter.	M. Merck.
18 C	.....	108	....	59.34	.....	59.13	.... 58.74
10 H	.....	10	....	5.49	.....	5.49	.... 5.62
8 O	.....	64	....	35.17	.....	35.38	.... 35.64
<hr/>							
$C^{18}H^{10}O^8$	.....	182	....	100.00	.....	100.00	.... 100.00

*Decompositions.* 1. The acid does not appear to be decomposed by strong nitric acid. (C. Merck.) It dissolves in *monohydrated nitric acid*, and is precipi-

tated by water as nitroveratric acid. (M. Merck.)—2. It does not appear to be decomposed by fuming oil of vitriol. (C. Merck.)—3. *Nitrosulphuric acid* gives it a fine yellow colour. (C. Merck.)—4. It is violently attacked by *bromine* and *chlorine*, forming uncrystallisable greasy substitution-products. (M. Merck.)—5. It does not appear to be altered by pentachloride of phosphorus. (M. Merck.)—6. Distilled with *baryta*, it is resolved into veratrol and carbonic acid. (M. Merck.)



**Combinations.** The acid dissolves sparingly in cold *water*, more readily in boiling water, separating out on cooling as a white crystalline powder.

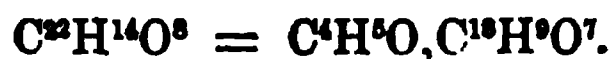
It combines with *bases*. The *potash* and *soda salts* are crystallisable, non-deliquescent, and soluble in water and alcohol. The ammonia-salt forms with *neutral acetate of lead*, a white precipitate soluble in water and in alcohol. (C. Merck.)

**Veratrate of Silver.**—Obtained by mixing the solution of the ammonia-salt with nitrate of silver, as a white bulky precipitate soluble in ammonia (Schrötter), also in water and in alcohol (C. Merck); it is decomposed by boiling water (Schrötter).

				Schrötter.	W. Merck. mean.
18 C	.....	108	....	37·36	..... 36·78
9 H	.....	9	....	3·11	..... 3·19
Ag	.....	108	....	37·39	..... 37·17
8 O	.....	64	....	22·14	..... 22·86
<hr/>				<hr/>	
$\text{C}^{18}\text{H}^9\text{AgO}^8$	.....	289·1	....	100·00	..... 100·00

Veratric acid dissolves in alcohol, very abundantly at the boiling heat. It is insoluble in ether.

### Veratrate of Ethyl.



WILL. *Ann. Pharm.* 37, 198.

*Veratric ether, Veratrumsäure-æther, Veratrum-vinester.*

A warm, moderately concentrated solution of veratric acid in strong alcohol is saturated with hydrochloric acid gas (if the solution is too strong, part of the acid separates out unaltered when the gas is passed through it); the hydrochloric acid and chloride of ethyl are distilled off, and the residue is mixed with water. Veratric ether then separates as a thick oil, which, after being washed with dilute carbonate of soda, gradually solidifies and may then be dried over oil of vitriol in vacuo.

**Properties.** Solid, radio-crystalline, easily friable mass. Crystallises from alcohol by spontaneous evaporation in shining needles united in

### 356 PRIMARY NUCLEUS $C^{18}H^{14}$ : OXYNITRO-NUCLEUS $C^{18}XH^9O^4$ .

stellate groups. Melts at  $42^\circ$  when heated under water, and solidifies on cooling. Sp. gr. 1.141 at  $18^\circ$ . Nearly inodorous; has a somewhat bitter slightly aromatic taste.

				Will.
22 C	132	...	62.86	62.85
14 H	14	...	6.66	6.62
8 O	60	...	30.48	30.53
<hr/>				
$C^4H^5O, C^{18}H^9O^7$	210	...	100.00	100.00

The ether cannot be volatilised without partial decomposition. Burns with a yellow flame when heated in the air. Gives off vapour of alcohol when heated with potash.

Nearly insoluble in water, easily soluble in alcohol.

*Oxynitro-nucleus*  $C^{18}XH^9O^4$ .

#### Nitroveratric Acid.



W. MERCK. *Compt. rend.* 47, 36.

*Formation* (p. 354).

Crystallises from alcohol in small yellow laminæ.

				M. Merck.
18 C	108	...	47.57	47.30
N	14	...	6.16	6.78
9 H	9	...	3.96	4.53
12 O	96	...	42.31	41.39
<hr/>				
$C^{18}XH^9O^8$	227	...	100.00	100.00

When boiled with concentrated *nitric acid*, it is converted into binitroveratric acid, which is difficult to separate from the nitroveratric acid.

Sparingly soluble in *water*, easily in *alcohol*.

#### Appendix.

#### Veratrol.



W. MERCK. *Compt. rend.* 47, 37.

*Formation* (p. 355).

When 1 part of veratric acid is gently heated in a retort with 3 parts of baryta, a violent action takes place and veratrol passes over.

*Properties.* Colourless oil having an agreeable aromatic odour, solidifying at 15° and boiling from 202° to 205°. Sp. gr. 1·086 at 5°.

*Decompositions.* 1. Veratrol is violently attacked by strong *nitric acid*, and converted, first into yellow laminæ of veratrol, afterwards into binitroveratrol. — 2. Bromine acts violently upon it, giving off hydrobromic acid, and converting it into a crystalline mass, from which bibromoveratrol may be separated by repeated crystallisation. If the action of the bromine be continued, uncrystallisable products are formed, richer in bromine. — 3. Chlorine acts like bromine, forming at first a crystallisable product, afterwards a greasy mass. — 4. It is not altered by pentachloride of phosphorus, weak acids, or hydrochloric acid. — 5. Potassium placed upon veratrol becomes surrounded with a jelly, without perceptible evolution of hydrogen. — 6. Veratrol is not altered by alkalis, by bisulphite of soda, or nitrate of silver.

### Binitroveratrol.



W. MERCK. *Compt. rend.* 47, 38.

*Formation* : see above.

Beautiful long yellow needles.

					M. Merck.
16 C .....	96	...	42·10	.....	41·22 to 42·31
2 N .....	28	...	12·28	.....	11·69
8 H .....	8	...	3·51	.....	3·46 to 4·02
12 O .....	96	...	42·11	.....	
<hr/>					
$\text{C}^{16}\text{X}^2\text{H}^2\text{O}^4$ .....	100	...	100·00		

### Bibromoveratrol.



W. MERCK. *Compt. rend.* 47, 38.

*Formation* : see above.

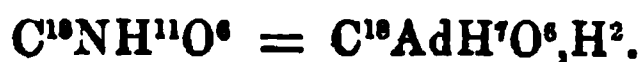
Crystallises from alcohol in fine prisms, which melt at 92°, and volatilise without decomposition at a higher temperature. They contain 54·17 p. c. Br. (Calc. 54·05 p. c.)

Insoluble in *water*. Easily soluble in *alcohol* and in *ether*.



*Oxyamidogen-nucleus*  $C^{15}AdH^7O^6$ .

### Tyrosine.



- LIEBIG. (1846.) *Ann. Pharm.* 57, 127; 62, 269.  
 WARREN DE LA RUE. *Phil. Mag. J.* 29, 145; *Ann. Pharm.* 64, 35;  
*Mem. Chem. Soc.* 3, 478.  
 BOPP. *Ann. Pharm.* 69, 20.  
 HINTERBERGER. *Ann. Pharm.* 71, 72.  
 STRECKER. *Ann. Pharm.* 73, 70.  
 PIRIA. *Ann. Pharm.* 82, 251.  
 ALEX. MÜLLER. *J. pr. Chem.* 57, 162.  
 LEYER u. KÖLLER. *Ann. Pharm.* 83, 332.  
 WITTSTEIN. *Vierteljahrsschrift f. pr. Pharmacie* 3, 348, 485; *Lieb. Kopp.*  
 1854, 656.  
 FRERICHS u. STÄDELER. *Müller's Archiv. für Anatomie und Physiologie*  
 1854, 382; *Chem. Centr.* 54, 861; *Lieb. Kopp.* 1854, 675; *Verhandl.*  
*der naturforsch. Gesellsch. in Zürich* iv, Juli, 1855; *Lieb. Kopp.*  
 1855, 729; *Müller's Archiv.* 1856, 37; *Lieb. Kopp.* 1856, 702.  
 R. HOFFMAN. *Ann. Pharm.* 87, 123.  
 GORUP-BESANEZ. *Ann. Pharm.* 98, 13.  
 SCHERER. *J. pr. Chem.* 70, 406.  
 C. WICKE. *Ann. Pharm.* 101, 314; *J. pr. Chem.* 71, 187.

From τυρός, cheese.

*Sources.* In cochineal. (De la Rue.) In the pancreas of man and of the lower animals. (Frerichs and Städeler.) Gorup-Besanez found tyrosine only once in the pancreas of the ox. In human liver (Scherer, *Virchow's Arch.* 10, 228, *Lieb. Kopp. Jahresber.* 1856, 708); not in healthy but in diseased liver, as in variola and typhus, in acute atrophy (in this case also in the urine); in the latter disease, the tyrosine separated in the crystalline form among the detritus of the disintegrated liver cells, as also in the liver of a woman who died of stoppage of the *ductus choledochus*, attended with comatose symptoms. (Frerichs and Städeler.) In the American *ratanhia-extract* a substance is found giving the reactions of tyrosine and containing the same amount of nitrogen. (Wittstein.)

*Formation.* By decomposing casein with hydrate of potash (Liebig), and fibrin or albumin with hydrate of potash, hydrochloric or sulphuric acid. (Bopp.) By melting ox-horn (Hinterberger), birds' feathers, hair, hedgehog-prickles, globulin or hæmatin (Leyer and Köller), with hydrate of potash, or by treating these substances with sulphuric acid. — It is formed in the putrefaction of yeast. Yeast kept for two or three months in open or in closed vessels was found to have entered into stinking putrefaction and liquefied to a brown mass, from which, in the case of *upper-yeast* (*Oberhefe*), many chalk-like tyrosine balls had deposited. Putrified *lower-yeast* (*Unterhefe*) deposited but little tyrosine on dilution with water, but after filtration crystals were obtained in abundance. (Alex. Müller.)

*Preparation. From Casein.* — Well pressed cheese, prepared from milk, either fresh or curdled, and freed as much as possible from adhering

butter, is fused with its own weight of hydrate of potash (or with solution of potash strong enough to crystallise on cooling) until hydrogen, as well as ammonia, is evolved from the melting mass; the mass is dissolved in hot water and slightly supersaturated with acetic acid; and the filtered liquid is left to cool, whereupon needles of tyrosine separate, which are purified by repeated solution in water containing carbonate of potash, and precipitation with acetic acid. (Liebig.) To purify it from leucine, when obtained in this manner, or according to preparation 5 of leucine (xi, 428), it is recrystallised from hot and then washed with cold water. It still retains some brown-red matter, to remove which, the solution in hydrochloric acid is treated with animal charcoal, decomposed with a quantity of acetate of potash equivalent to the amount of hydrochloric acid, and rapidly filtered (hot? Gm.), whereupon the filtrate becomes filled with entangled needles. A portion of the tyrosine remains dissolved in the acetic acid, but the rest is thereby freed from ash which adheres obstinately to the tyrosine crystallised from neutral solutions. The needles are washed with cold water, and once more crystallised. (Bopp.)

*From Horn.* — 1. One part of horn-shavings is boiled in a flask with 4 parts of oil of vitriol and 12 parts of water for 36 hours, the water being replaced as it evaporates; the liquid is supersaturated with milk of lime; the paste boiled for 24 hours in an iron pot; and the contents are discharged into a large linen filter, left to drain, and afterwards pressed. The turbid liquid is heated to boiling, and sulphuric acid is added till it reddens litmus; it is then filtered, precipitated with a mixture of neutral acetate of lead and a little basic acetate until all the sulphuric acid used in excess is combined with lead; afterwards boiled, filtered, treated with sulphuretted hydrogen, heated with the precipitated sulphide of lead, and again filtered; and the slightly coloured filtrate is evaporated to the crystallising point. The mother-liquor is decanted from the resulting crystals, and further evaporated as often as it yields crystals. The whole of the crystals are pressed between paper, washed with alcohol of 86 p. c., then with a little water, and boiled with water containing a very small quantity of potash and carbonate of potash; the liquid is filtered from the carbonate of lime; acetic acid added to the filtrate until it exhibits an acid reaction; the liquid cooled to the crystallising point; and the product recrystallised from boiling water with the aid of animal charcoal, until all inorganic matter is removed. 1 lb. horn yields 5 grammes of tyrosin. (Hinterberger.)

2. To a mixture of 3 litres of water and 1300 grms. of oil of vitriol, heated nearly to boiling, 500 grms. of horn-shavings are gradually added; and the whole is boiled for 48 hours, then diluted with water and neutralised with hydrate of lime. The filtrate is boiled for an hour or two with milk of lime, to remove a substance containing sulphur and a colouring matter, then filtered, and evaporated at a temperature near the boiling point till only  $2\frac{1}{2}$  — 3 litres of fluid remain, carbonic acid being continuously passed through it to precipitate the lime (the precipitation taking place but slowly); after which the liquid is again filtered and set aside till the next day, the tyrosine then crystallising out. The mother-liquor on further evaporation, yields an additional quantity, but mixed with leucine. Should the liquid not deposit any tyrosine, it must be again heated, and carbonic acid once more passed through it as long as carbonate of lime continues to separate. (Piria.) C. Wicke uses less oil

of vitriol [how much?]; boils for 24 hours only; removes the free sulphuric acid by lime; then concentrates the liquid and precipitates the lime by oxalic acid; removes the free sulphuric [oxalic?] acid with a small quantity of oxide of lead; and precipitates the lead by sulphuretted hydrogen: the precipitated sulphide of lead serves at the same time to remove colouring matter.

*From Cochineal.* — Decoction of cochineal is precipitated by neutral acetate or basic nitrate of lead; the liquid is filtered from the carminate of lead, and treated with sulphuretted hydrogen; and the filtrate is evaporated to a syrup, whereupon a chalk-like substance separates. This is washed with cold water, and several times recrystallised from boiling water, ultimately with the aid of animal charcoal. The separated crystals, which have a silky lustre, shrink on the filter to a paper-like mass, also having a silky lustre. 300 parts of cochineal yield 1 part of tyrosine. (De la Rue.)

*Properties.* Snow-white needles having a silky lustre (pearly, according to Bopp) (Liebig), or a conglomerated silky mass (paper-like after drying, according to De la Rue), composed of slender needles grouped in stars. (Hinterberger.) Thin, delicate, double tufts. (Scherer.) Very bulky. (Bopp.)

De la Rue. Hinterberger.								Leyser & Köller.		Müller.	
18 C .....	108	...	59.66	.....	59.41	...	59.36	...	59.14	...	59.54
N .....	14	...	7.73	.....	7.66	...	7.88	...		...	7.95
11 H .....	11	...	6.07	.....	6.29	...	6.24	...	6.12	...	6.58
6 O .....	48	...	26.54	.....	26.64	...	26.52	...		...	25.93
<hr/>											
C <sup>18</sup> NH <sup>11</sup> O <sup>6</sup> ...	181	...	100.00	.....	100.00	...	100.00	...		...	100.00

Belongs according to Städeler, to the salicine series, and is perhaps  $C^4H^5NO_4$  +  $C^{14}H^8O^4, 2HO$ : consequently glyocol-saligenin. (Frerichs and Städeler.)

Müller analysed tyrosine still containing 1.99 p. c. of ash, which was deducted in the calculation.

*Decompositions.* 1. Tyrosine is decomposed by *heat*, evolving an empyreumatic animal odour. (Bopp.) — 2. *It burns* without residue on platinum foil, emitting an odour of burnt hair. (Hinterberger.) — 3. With *oil of vitriol*, it forms tyrosine-sulphuric acid, the neutral salts of which colour sesquichloride of iron violet. If tyrosine be placed on a watch-glass; one or two drops of sulphuric acid added; the mixture covered and set aside for half an hour, and then diluted with water; the acid saturated by boiling with carbonate of lime, and the liquid filtered: the filtrate gives with a few drops of a neutral solution of sesquichloride of iron, a rich violet colour, similar to the coloration produced by salicylous acid. (Piria.) Tyrosine acquires a transient red colour when oil of vitriol is poured upon it; if the liquid be heated for some time to  $200^\circ$ , then diluted with water and neutralised with baryta, the filtrate yields on evaporation an amorphous and a crystalline salt of tyrosine-sulphuric acid, the former dissolving readily the latter with difficulty in cold water. (Frerichs and Städeler.) — 4. It dissolves in *bromine water*, which it decolorises; on evaporation a brown crystalline residue remains; the solution when distilled becomes brown, and yields a milky distillate having an odour

slightly resembling that of bitter almond-oil. (C. Wicke.) — 5. Tyrosine is transformed by moist *chlorine* into an uncrystallisable resin, readily soluble in absolute alcohol. (Wicke.) — 6. Suspended in water, it dissolves, with evolution of gas, when nitrous acid is passed into the liquid; the pale yellow solution, neutralised with carbonate of baryta and freed from excess of baryta, deposits on evaporation a reddish yellow salt, which, after drying over oil of vitriol, still gives off 7.1 p. c. of water at 100°, and then contains 57.8 p. c. Ba. (Wicke.) — 7. Dissolves in *nitric acid* with evolution of gas; the solution leaves on evaporation crystals of a peculiar acid (De la Rue); oxalic acid. (Strecker.) If the nitric acid becomes heated, a violent action sets in, often attended with separation of charcoal and destruction of the acid. (De la Rue.) Common nitric acid rapidly dissolves tyrosine, forming a yellow solution, red fumes beginning to escape after a few moments; nitrate of nitrotyrosine then separates as a yellow, crystalline powder. Boiling nitric acid forms oxalic acid only. (Strecker.) Tyrosine evaporated on platinum foil with nitric acid of sp. gr. 1.2 dissolves with bright orange colour; on evaporating the liquid, a brilliant, transparent, deep yellow residue remains, which becomes deep reddish yellow when moistened with solution of soda, and black-brown when evaporated with it. (Scherer.) — 8. Mixed with *hydrochloric acid* and *chlorate of potash*, it yields a red solution which gives off gas and turns yellow, and from which a substance separates smelling of chlorochinone and insoluble in water. (Städeler.) — 9. Tyrosine boiled with dilute sulphuric acid and *peroxide of lead*, is decomposed slowly, with evolution of carbonic acid; the filtered liquid freed from the sulphuric acid by carbonate of baryta, yields, after concentration and addition of absolute alcohol, a dark amorphous precipitate, and when filtered from this and evaporated, a few microscopic right-angled prismatic crystals. (Wicke.) — 10. Tyrosine boiled with mercuric nitrate (not too acid) is precipitated in red flakes, while the supernatant clear liquid assumes a dark rose red colour, and then, on standing, becomes colourless, with a second deposition of red flakes. Boiling nitric acid dissolves the precipitate and decolorises the solution; neutralisation does not restore the colour. By this test, tyrosine may be recognised in a solution containing less than  $\frac{1}{950}$  part. (Hofmann.)

*Combinations.* Dissolves with difficulty in water (Liebig), sparingly in cold, abundantly in hot water. (De la Rue; Hinterberger.)

Tyrosine combines with acids. (Liebig.) It dissolves readily in hydrochloric acid (De la Rue), and in dilute sulphuric acid (Bopp), in mineral acids (Hinterberger); the solutions may be evaporated at 100° without decomposition (Bopp), the solution in hydrochloric acid (in volatile acids, according to Strecker), leaving tyrosine (free from acid) in moderately large crystals. (De la Rue.)

*Hydrochlorate of Tyrosine.* — 1. Tyrosine dried at 100° absorbs 16.78 p. c. of its own weight of dry hydrochloric acid when that gas is passed over it. — 2. A moderately concentrated solution of tyrosine in hydrochloric acid solidifies when mixed with an excess of fuming hydrochloric acid, to a pulp of needle-shaped crystals. — 3. The solution of tyrosine in concentrated hydrochloric acid, saturated when warm, deposits on cooling hydrochlorate of tyrosine, which may also be obtained in well formed, hard crystals, by spontaneous evaporation of the solution in the air or over oil of vitriol. (Wicke.)

					Wicke. mean.
$C^{18}NH^{11}O^6$	.....	181	...	83.24	
HCl	.....	36.5	...	16.76	..... 16.74
<hr/>					
$C^{18}NH^{11}O^6, HCl$	....	217.5	....	190.00	

Tyrosine dissolves in ammonia and on evaporation remains in rather large crystals (De la Rue, Hinterberger), in balls made up of pure white needles and appearing jagged on the surface, in consequence of small crystals projecting from the balls. (Scherer.)

It dissolves readily in alkalis (Liebig), and is precipitated by acids. (De la Rue.)

It dissolves readily in the alkaline earths, forming combinations with them. The solutions obtained by heating an excess of tyrosine with baryta-water or milk of lime, crystallise when rapidly evaporated. (The lime-compound was once found to contain 10.11 p. c. Ca: calculation  $C^{18}NH^{10}O^6Ca = 10.0$  p. c.; but its composition and likewise that of the baryta-compound varied in different preparations.) Water seems to decompose these compounds. (Wicke.)

Tyrosine does not dissolve in absolute alcohol (Liebig), scarcely (Bopp), more in presence of acids or alkalies (Strecker).

It does not dissolve in ether. (Hinterberger.)

### Tyrosine-sulphuric Acid.

FRERICHS u. STÄDELER. *Müller's Archiv. für Anat. u. Physiologie* 1854, 387; *Chem. Centr.* 1854, 861; *Lieb. Kopp. Jahresber.* 1854, 675.

The solution of tyrosine-sulphate of baryta, obtained as already described (p. 360), by the action of oil of vitriol on tyrosine, forms a gelatinous mass on cooling, and is resolved by treatment with alcohol, into a crystallisable and an amorphous salt.

*a. Crystalline Salt.* —  $C^{18}H^9NO^6, BaO, SO^3 + BaO, SO^3 + Aq.$  (Frerichs and Städeler.) Loses 2 At. water at  $100^\circ$ . When heated it turns brown, chars, and evolves the odour of sulphuretted hydrogen and of ammonia. Dissolves with difficulty even in hot water. Dissolves readily in mineral acids; in oil of vitriol without disengagement of sulphuretted hydrogen. Its aqueous solution is coloured violet by sesquichloride of iron. Dissolves readily in acetic acid, the solution soon depositing hard crystalline grains.

*b. Amorphous Salt.* —  $C^{18}H^9NO^6BaO, S^2O^3 + BaO, SO^3$ . (Frerichs and Städeler.) Separates in a gelatinous mass on the evaporation of its aqueous solution. Loses 2 At. water when heated to  $100^\circ$ ; when further heated it evolves sulphuretted hydrogen, ammonia, and a small quantity of sulphur. Dissolves in oil of vitriol with evolution of sulphuretted hydrogen. Dissolves in acetic acid, the solution leaving on evaporation a residue from which water or alcohol extracts acetate of baryta and leaves small plates and prisms.

Readily soluble in cold water. Soluble in nitric acid.

*Oxynitroamidogen-nucleus*  $C^{18}AdXH^6O^6$ .

### Nitrotyrosine.



STRECKER. *Ann. Pharm.* 73, 70.

#### *Formation of the Nitrate.*

*Preparation.* The compound of nitrotyrosine with oxide of silver is suspended in water and decomposed by sulphuretted hydrogen, and the filtrate is evaporated.

Light-yellow crystals, consisting of microscopic needles grouped in stars. Explodes when heated. Does not exhibit the reaction of nitric acid with protosulphate of iron and sulphuric acid.

*Sulphate of Nitrotyrosine.* — Nitrate of nitrotyrosine with sulphuric acid evolves nitric acid, and leaves on evaporation crystals of sulphate of nitrotyrosine.

*Hydrochlorate of Nitrotyrosine.* — Yellow needles, which are obtained by decomposing the compound of nitrotyrosine and oxide of silver with hydrochloric acid.

*Nitrate of Nitrotyrosine.* — Tyrosine is suspended in water, nitric acid added by drops till the resulting solution has acquired a yellow colour, no disengagement of gas taking place; it is then left at rest. After several hours, sooner if the glass be rubbed with a glass rod, the nitrate of nitrotyrosine deposits almost completely as a yellow crystalline powder, which is purified by recrystallisation from boiling water.

Brown, almost bronze-like scales, which give a light-yellow powder. After drying over oil of vitriol, it does not lose weight at 100°; at 125° it loses in 8 hours 0.5 p. c. of its weight. Tastes bitter; its solution reddens litmus.

					Strecker. mean.
18 C .....	108	...	37.37	.....	37.55
3 N .....	42	...	14.53	.....	14.37
11 H .....	11	...	3.81	.....	4.05
16 O .....	128	...	44.29	.....	44.03
$C^{18}NXH^{10}O^6, HO, NO^3$ ....					289
					100.00
					100.00

Nitrate of nitrotyrosine dissolves in baryta-water, forming a reddish brown solution from which the baryta is not completely precipitated by carbonic acid. On boiling with carbonate of baryta, a yellow solution is obtained, which when evaporated leaves two kinds of crystals (probably nitrate of baryta and nitrotyrosine-baryta. Gm.). Alcohol produces a red precipitate in the solution. The salt dissolves but sparingly in cold water, more readily in boiling water. It dissolves in ammonia or potash with very-deep-red colour. The aqueous solution gives the nitric acid reaction with protosulphate of iron and sulphuric acid.



The solution of nitrotyrosine in ammonia forms an orange precipitate with neutral acetate of lead; greenish yellow with acetate of copper; greenish white with mercurous nitrate; and light-yellow with corrosive sublimate.

*Nitrotyrosine with Oxide of Silver.*—Nitrate of nitrotyrosine dissolved in dilute ammonia forms with nitrate of silver, in the cold, a yellow amorphous precipitate, which becomes bright-red on boiling and dirty-brown with excess of ammonia. Explodes feebly when heated. Dissolves in nitric acid and in ammonia.

Yellow compound dried over oil of vitriol.					Strecker. mean.
36 C	.....	216	....	27.94	..... 28.25
4 N	.....	56	....	7.25	
17 H	.....	17	....	2.20	..... 2.34
3 Ag	.....	324	....	41.92	..... 41.56
20 O	.....	160	....	20.69	
<hr/>					
$C^{15}N^4H^{17}O^{17}, 3AgO$ .....					773 .... 100.00
$C^{15}NXH^9AgO^6 + C^{15}NXH^8Ag^2O^6$ . (Gm.)					

Nitrotyrosine dissolves sparingly in cold *alcohol*, somewhat more in hot *alcohol*, but less than in *water*.

#### *Azo-nucleus* $C^{15}N^4H^{10}$ .

#### Hydrocyanaldine.



A. STRECKER. *Ann. Pharm.* 91, 349; *J. pr. Chem.* 62, 441.

When an aqueous solution of aldehyde and ammonia is mixed with prussic and dilute hydrochloric acid, so that the mixture has a distinctly acid reaction, and then set aside in closed vessels, colourless needles separate after some time, more especially in sunlight, filling up the liquid, and are obtained pure and free from hydrochloric acid by washing with a little cold water. On the cooling of the aqueous solution saturated while boiling, it separates in colourless scales; from a dilute solution it slowly crystallises in needles. When carefully heated, it melts and sublimes without decomposition. Tasteless. Neutral.

					Strecker.
18 C	.....	108	....	61.4	..... 61.15
4 N	.....	56	....	31.8	..... 32.00
12 H	.....	12	....	6.8	..... 6.85
<hr/>					
$C^{15}N^4H^{12}$ .....					176 .... 100.0 ..... 100.00



When rapidly heated, it decomposes, chars and evolves an odour similar to that of prussic acid. Aqueous hydrocyanaldine is not precipi-

tated by nitrate of silver, not even on addition of nitric acid, but when heated with it to boiling, it deposits cyanide of silver and evolves the odour of aldehyde. It is not decomposed by cold potash, but boiling potash decomposes it, with evolution of ammonia and separation of aldehyde resin.

Hydrocyanaldine dissolves abundantly in boiling *water* and separates again almost entirely on cooling. It dissolves readily in *alcohol*, sparingly in *ether*.

*Primary Nucleus*  $C^{18}H^{16}$ .

**Campholene.**  $C^{18}H^{16}$ .

DELALANDE. *N. Ann. Chim. Phys.* 1, 125; *J. pr. Chem.* 23, 391; *Ann. Pharm.* 38, 340.

Camphoric acid is distilled with anhydrous phosphoric acid and the distillate is rectified.

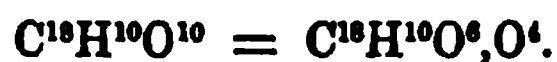
Oil, which boils steadily at  $135^{\circ}$ . Vapour-density = 4.353.

					Delalande.
18 C .....	108	...	87.09	.....	87.25
16 H .....	16	...	12.91	.....	12.80
<hr/>					
$C^{18}H^{16}$ .....	124	...	100.00	.....	100.05

		Volume.	Density.
C-vapour .....	18	.....	7.4880
H-gas .....	12	.....	0.8316
<hr/>			
Campholene-vapour.....	2	.....	8.3196
	1	.....	4.1598

*Oxygen-nucleus*  $C^{18}H^{10}O^6$ .

**Apoglucic Acid.**



MULDER. *J. pr. Chem.* 21, 230.

*Formation.* From glucic acid by boiling the aqueous solution in the air or with dilute acids. By the evaporation of glucate of lime in the air.

*Preparation.* See glucic acid (p. 238, 3). The brownish flakes precipitated by alcohol collect on the filter in a brownish jelly, which darkens in



drying. This mass is apoglucate of lime, which must be dissolved in a little water to separate admixed sulphate of lime, then filtered, and either evaporated or precipitated by alcohol. To obtain the acid, the solution of the lime-salt is precipitated by neutral acetate of lead, the precipitate decomposed with sulphuretted hydrogen, and the filtrate evaporated to dryness.

*Properties.* The acid has a fine brown colour and, generally, a crystalline texture. It is permanent in the air. According to Mulder, it probably retains 1 At. of water at  $120^{\circ}$ .

	At $120^{\circ}$ .			Mulder.	
18 C .....	108	...	54.54	.....	53.36
10 H .....	10	...	5.05	.....	5.42
10 O .....	80	...	40.41	.....	41.22
<hr/>					
$C^{18}H^{10}O^{10}$ .....	198	...	100.00	.....	100.00

According to Mulder, it is  $C^{18}H^{11}O^{10}$ ; according to Gerhardt, it is perhaps identical with assamar,  $C^{24}H^{12}O^{12}$  (*Traité* 2, 565). The formula given above was proposed by Vöckel. (*Ann. Pharm.* 85, 86.)

*Decompositions.* 1. When subjected to *dry distillation*, it does not swell up, but emits an odour of burnt paper, and yields an acid distillate which is free from ammonia.

2. It is decolorised by concentrated *nitric acid* and decomposed with abundant evolution of nitrous acid: the solution contains oxalic acid.

3. Dissolves in cold *oil of vitriol* with blood-red colour.

4. *Chlorine* passed through apoglucate of lime produces formic acid, decolorises the solution, and precipitates a red powder, of the same colour as that furnished by humic acid.

Apoglucic acid dissolves readily in *water* and is not precipitated by alcohol. It dissolves without decomposition in dilute *sulphuric acid* and in concentrated *hydrochloric acid*.

Dissolves with dark-red colour in *ammonia*, *potash*, *soda*, and *baryta* or *lime water*.

*Apoglucate of Lime.* — Brown, amorphous mass. May be pulverized, does not become moist in the air. The aqueous solution may be perfectly decolorised by bone-black, and is then no longer precipitated by basic acetate of lead, because the charcoal has taken up all the lime-salt. It is insoluble in alcohol.

	Dried at $130^{\circ}$ .			Mulder.	
18 C .....	108	...	49.77	.....	49.19
9 H .....	9	...	4.14	.....	4.74
9 O .....	72	...	33.18	.....	33.02
CaO .....	28	...	12.91	.....	13.05
<hr/>					
$C^{18}CaH^9O^{10}$ .....	217	...	100.00	.....	100.00

*Apoglucate of Lead.* — The alkaline apoglucates form with lead-salts a brown gelatinous precipitate which dissolves to a certain extent during washing.

<i>Dried at 130°.</i>				<b>Mulder.</b>	
18 C	.....	108	...	35.94	..... 36.27
9 H	.....	9	...	2.99	..... 3.09
9 O	.....	72	...	28.93	..... 21.98
PbO	.....	111.8	...	37.14	..... 38.66
<hr/>					
C <sup>18</sup> PbH <sup>9</sup> O <sup>10</sup>	.....	300.8	...	100.00	..... 100.00

Free apoglucic acid and its alkaline salts precipitate *acetate of copper* brown.

*Apoglucate of Silver.*—The alkaline apoglucates form with silver-salts a brown gelatinous precipitate, which gradually dissolves during washing. Dark mass, having a metallic lustre.

					Mulder.
$C^{18}H^9O^9$ .....	189	...	61.95	.....	60.7
$AgO$ .....	116.1	...	38.05	.....	39.3
<hr/>					
$C^{18}AgH^9O^{10}$ .....	305.1	...	100.00	.....	100.0

Apoglucic acid is sparingly soluble in *alcohol*; insoluble in *ether*. (Mulder.)

### Primary Nucleus C<sup>18</sup>H<sup>18</sup>.

### Pelargonene. C<sup>18</sup>H<sup>18</sup>.

E. FREMY. (1837.) *Ann. Chim. Phys.* 65, 143.

*Elaene, Nonylene, Gona.*

*Formation and Preparation.* From the mixture obtained by the dry distillation of hydroleic acid or metoleic acid, according to xi, 411, the more volatile pelargonene is removed by heating for some time at 100°; it is then several times distilled over potash to remove empyreumatic oil. It should disappear completely without leaving a residue, when left to evaporate on a glass-plate.

Colourless oil, floating on water, boiling at 110°. Vapour density = 4.488 (other experiments with very well purified oil gave 4.071). Has a penetrating odour, somewhat different from that of caproene.

						Fremy.
18 C .....	108	...	85.71	.....	84.26	
18 H .....	18	...	14.29	.....	14.64	
<hr/>						
C <sup>18</sup> H <sup>12</sup> .....	126	...	100.00	.....	98.90	

	Volume.	Vapour density.
C-vapour .....	18 .....	6.6506
H-gas .....	18 .....	1.1088
<hr/>		
Pelargonene-vapour ....	2 .....	7.7594
	1 .....	3.8797

*Burns* with a white flame. Does not appear to be decomposed by *oil of vitriol*. Transformed by *chlorine gas* into chloride of pelargonene.

Insoluble in *water*.

Dissolves in *alcohol* less abundantly than caproene, also in *ether*.

### Naphtene. $C^{18}H^{18}$ .

LAURENT. (1837.) *Ann. Chim. Phys.* 64, 321; *Ann. Pharm.* 25, 283; *J. pr. Chem.* 11, 418.

The colourless oil, obtained by treating the empyreumatic oil from shale with concentrated nitric acid (xii, 442) and whose boiling point lies between  $120^{\circ}$  and  $122^{\circ}$ , is repeatedly purified with oil of vitriol and potash.

Limpid, very fluid. Sp. gr. 0.753 at  $12^{\circ}$ . Smells very acrid.

					Laurent.
18 C	.....	108	....	85.71	..... 86.2
18 H	.....	18	....	14.29	..... 13.6
<hr/>					
$C^{18}H^{18}$	.....	126	....	100.00	..... 99.8

With chlorine, when exposed to the sun, it yields hydrochloric acid; afterwards small isolated crystals containing chlorine. Not changed by hydrochloric acid, oil of vitriol, or nitric acid.

### Bichloride of Pelargonene. $C^{18}H^{18}, Cl^2$ .

FREMY. *Ann. Chim. Phys.* 65, 145.

*Chlorure d'elaène, Chlorure de nonylène, Zweifach-chlorgone.*

When a stream of chlorine is passed through pelargonene contained in a retort, the gas is absorbed with rise of temperature and evolution of hydrochloric acid. The product is heated in chlorine gas and distilled.

Denser than water. Of a rather agreeable odour, like that of anise.

					Fremy.
18 C	.....	108	....	54.87	..... 54.89
18 H	.....	18	....	9.14	..... 9.05
2 Cl	.....	70.8	....	35.99	..... 35.27
<hr/>					
$C^{18}H^{18}Cl^2$	.....	196.8	....	100.00	..... 99.21

Burns with a green, fuliginous flame.

# Pelargonic Acid.



REDTENBACHER. (1846.) *Ann. Pharm.* 59, 52.

PLESS. *Ann. Pharm.* 59, 54.

GERHARDT. *Compt. rend.* 26, 226; *N. J. Pharm.* 14, 148; *N. Ann. Chim. Phys.* 24, 107; *Ann. Pharm.* 67, 245.

CAHOURS. *Compt. rend.* 26, 262; 31, 143; *Qu. Chem. Soc. J.* 3, 240.

CHIOZZA. *Compt. rend.* 35, 797; *N. Ann. Chim. Phys.* 39, 207; *Ann. Pharm.* 85, 225.

The volatile oil of *Pelargonium roseum* was prepared in 1827, by Recluz (*J. Pharm.* 13, 529; *Mag. Pharm.* 20, 140); Pless (1846) discovered in it the pelargonic acid, which was simultaneously obtained by Redtenbacher, by the oxidation of oleic acid, and by Cahours and Gerhardt, by the oxidation of oil of rue.

According to Delffs, oenanthic acid (xii, 455) is identical with pelargonic acid.

*Sources.* In the volatile oil of *Pelargonium roseum*. (Pless.)

*Formation.* 1. Pelargonic acid is produced, together with several other volatile acids, in the distillation of choloidic and of oleic acid with nitric acid. (Redtenbacher.) See Oleic acid. — 2. In the oxidation of oil of rue by nitric acid. (Gerhardt; Cahours.) — 3. A small quantity of pelargonic acid is formed, together with many other volatile acids, in the putrefaction of yeast. (W. Muller. *J. pr. Chem.* 70, 66); O. Hesse. *J. pr. Chem.* 71, 472.)

*Preparation.* *From oil of rue.* — When 1 pt. of oil of rue is gently heated with 1 pt. of commercial nitric acid and 2 pts. of water, an action sets in, violent at first and continuing for a quarter or half an hour, even after the fire has been removed. The liquid is then boiled and cohobated repeatedly, till scarcely any red fumes are evolved; the layer of oil is decanted, washed with water, and treated with aqueous potash, whereupon some non-acid oil of a very acrid odour is separated; the alkaline solution is decomposed by sulphuric acid; and the oily acid which separates, and is contaminated with resin and colouring matters, is collected and rectified. The distillate is neutralised with baryta, freed from excess of baryta with cold water, dissolved in boiling alcohol, then filtered and cooled to the crystallising point. Pelargonate of baryta then crystallises out (the mother-liquor sometimes retains caprate of baryta), and this salt decomposed with dilute sulphuric acid, yields pelargonic acid as an oil floating on the surface. (Gerhardt.) Owing to certain circumstances not ascertained, a compound of nitric oxide with pelargonic acid is sometimes obtained in this process. (Chiozza.)

*From the blossoms and herb of Pelargonium roseum.* — The herb is distilled with water; the distillate saturated with baryta; the neutral oil distilled off; and the residue evaporated to dryness and extracted with boiling alcohol, which takes up pelargonate of baryta. (Pless.)

*Properties.* Colourless oil (greasy according to Redtenbacher), which solidifies in the cold, melting afterwards at 10°. Smells slightly of butyric acid. Boils at 260°; in a stream of carbonic acid gas it distils undecomposed and colourless. (Cahours.)

**Decompositions** 1. Becomes yellow in time. (Cahours.) — 2. When 1 pt. of pelargonic acid is intimately mixed with 4 pts. of *potash-lime*, and gradually raised to a red heat in a coated retort, much gas escapes, a clear, amber-yellow, thin liquid passes over, and the alkali, partly combined with carbonic acid, remains behind. Bromine absorbs the greater part of the gas composed of ethylene, propylene and butylene; the undensed portion burns with a very faint flame and is a mixture of hydrogen and marsh gas. The liquid, during rectification, begins to boil at  $105^{\circ}$  to  $106^{\circ}$ ; up to  $110^{\circ}$  caprylene (p. 180) passes over; then to  $135^{\circ}$ , and at last to  $140^{\circ}$ , the remainder. (Cahours.) — 3. The acid is resolved by the dry *distillation* of its baryta-salt into carbonate of baryta and pelargone. (Cahours.) — 4. It is violently acted upon by *pentachloride of phosphorus*, evolving hydrochloric acid and forming chlorophosphoric acid and chloride of pelargyl. (Cahours.)

**Combinations.** Pelargonic acid dissolves with great difficulty in water (Redtenbacher); it is scarcely soluble in water; the solution reddens litmus. (Gerhardt.)

**Pelargonate of Ammonia.** — Crystallises. (Cahours.) Pelargonic acid suspended in ammonia and heated, forms a transparent jelly resembling gelatinous silica. This jelly dissolves when heated with a larger quantity of water, and forms a milky liquid, resembling a solution of soap, and congealing in the cold to a pap-like jelly. The salt dissolves very readily in cold alcohol. (Gerhardt.)

**Pelargonate of Potash and Pelargonate of Soda,** are readily soluble and crystallise. (Cahours.)

**Pelargonate of Lime** crystallises from boiling alcohol in pearly scales. Dissolves with difficulty in water. (Cahours.)

**Pelargonate of Baryta.** — *Preparation* (p. 369.) White scales, having a pearly lustre (Gerhardt); large laminæ resembling cholesterin. (Redtenbacher.) Contains no water of crystallisation. Dissolves but sparingly in cold, somewhat more in hot water (Gerhardt); dissolves in water less readily than the similarly crystallising valerate and œnanthylate of baryta, but more readily than caprate of baryta. Dissolves with difficulty in alcohol. (Redtenbacher.)

	At $110^{\circ}$ .			Redtenbacher.	
BaO.....	76.6	...	33.99	.....	33.86
18 C .....	108	...	47.85	.....	47.34
17 H .....	17	...	7.54	.....	7.46
3 O .....	24	...	10.62	.....	11.34
<hr/>					
$C^{18}BaH^{17}O^4$ .....	225.6	...	100.00	.....	100.00

Contains at  $100^{\circ}$ , 33.79 p. c. baryta (Gerhardt); 33.65 p. c. (Chiozza).

**Pelargonate of Strontia.** — Pearly scales. Dissolves but sparingly in water. (Gerhardt.)

**Pelargonate of Copper.** — The alcoholic ammonia-salt is precipitated by aqueous nitrate of copper. The abundant, greenish blue precipitate

dissolves in boiling alcohol and on evaporation yields drops of a green oil which solidify on cooling, and when dissolved in boiling alcohol crystallise in greenish blue grains on cooling. When dried at 100°, it contains 2 At. water of crystallisation.

At 100°.				Gerhardt.
C <sup>18</sup> H <sup>17</sup> O <sup>4</sup> .....	157	....	75.92	
Cu.....	31.8	....	15.38	..... 15.45
2 Aq.....	18	....	8.70	
<hr/>				
C <sup>18</sup> CuH <sup>17</sup> O <sup>4</sup> , + 2Aq .....	206.8	....	100.00	

*Pelargonate of Silver.* — The hot aqueous solution of the baryta salt is precipitated with nitrate of silver, and the white and very bulky precipitate is washed with boiling water.

				Redtenbacher.	Pless.	Gerhardt.
				At 100°.		At 160°.
18 C .....	108	....	40.75	..... 39.98	.... 40.88	.... 40.3
17 H .....	17	....	6.42	..... 6.33	.... 6.41	.... 6.4
Ag .....	108.1	....	40.75	..... 41.16	.... 40.74	.... 40.8
4 O .....	32	....	12.08	..... 12.53	.... 11.97	.... 12.5
<hr/>						
C <sup>18</sup> AgH <sup>17</sup> O <sup>4</sup> .....	265.1	....	100.00	..... 100.00	.... 100.00	.... 100.0

Pelargonic acid is readily soluble in *alcohol* and *ether*. (Redtenbacher.)

## Nitroso-pelargonic Acid.



CHIOZZA. *Compt. rend.* 35, 797; *Ann. Pharm.* 85, 225.

### *Stickoxyd-pelargonsäure.*

*Formation and Preparation.* 1 pt. oil of rue is boiled for three or four hours with 1 pt. commercial (or pure) nitric acid and 1 pt. water; and the layer of oil floating on the acid is then removed, washed with water, and treated with a concentrated solution of potash, whereby a considerable rise of temperature is occasioned and a syrupy, highly coloured emulsion produced, holding in suspension a crystalline precipitate, the quantity of which is further increased on addition of water. The precipitate of nitroso-pelargonate of potash is filtered from the solution containing pelargonic acid, washed with ether to remove a neutral oil, and crystallised from alcohol. The crystals dissolved in boiling water and decomposed by a dilute mineral acid, yield nitroso-pelargonic acid as an oil, which is washed with boiling water and dried in the water-bath.

*Properties.* Slightly yellow oil denser than water. Has a faint odour, different from that of pelargonic acid. Produces a yellow stain on linen, and a greasy stain on paper, which vanishes when slightly heated.

					Chiozza.
18 C	.....	108	...	49.5	..... 49.5
2 N	.....	28	...	12.8	..... 13.3
18 H	.....	18	...	8.2	..... 8.4
8 O	.....	64	...	29.5	..... 28.8
<hr/>					
$C^{18}N^2H^{18}O^8$	.....	218	...	100.0	..... 100.0

Heated in a tube, it suddenly evolves nitric oxide and inflammable gases in large quantities.

*Combinations.* All the salts of *nitroso-pelargonic acid* dissolve with great difficulty in cold water.

*Nitroso-pelargonate of Ammonia.*—Lustrous, elongated scales. Paper soaked in the acid turns yellow and opaque when dipped in ammonia diluted with 1000 pts. of water.

*Nitroso-pelargonate of Potash.*—*Preparation* (p. 371). Four-sided, rectangular plates, having a fine yellow colour and very high lustre. When heated, it explodes like nitre mixed with charcoal, and leaves carbonate of potash. It is very sparingly soluble in cold water, readily in boiling water and alcohol.

*Nitroso-pelargonate of Soda.*—Similar to the potash salt. Separates almost entirely on the cooling of its solution saturated while boiling.

*Nitroso-pelargonate of Baryta.*—Obtained by double decomposition. Yellow, very light powder.

					Chiozza.
$C^{18}H^{17}O^4, 2NO^2$	.....	217	...	76.01	
Ba	.....	68.5	...	23.99	..... 23.3
<hr/>					
$C^{18}H^{17}BaO^4, 2NO^2$	.....	285.5	...	100.00	

*Nitroso-pelargonate of Silver.*—Resembles the baryta-salt. When heated, it ignites, burns with a greenish flame, and leaves metallic silver.

					Chiozza.
$C^{18}H^{17}O^4, 2NO^2$	.....	217	...	66.75	
Ag	.....	108.1	...	33.25	..... 33.6
<hr/>					
$C^{18}H^{17}AgO^4, 2NO^2$	.....	325.1	...	100.00	

### Pelargonate of Ethyl.

$$C^2H^2O^4 = C^4H^6O, C^{18}H^{17}O^3.$$

CAHOURS. *Chem. Soc. Qu. J.* 3, 240.

*Pelargonic ether, Pelargonvinester.*

*Formation and Preparation.* 1. From chloride of pelargyl and alcohol (p. 377).—2. When hydrochloric acid gas is passed through

alcoholic pelargonic acid, the ether separates as a yellow oil which is washed successively with carbonate of soda and water, dried over chloride of calcium, and rectified.

Colourless oil of sp. gr. 0·86. Boils at 216°—218°. On boiling with potash it is resolved into alcohol and pelargonate of potash.

### Pelargonic Anhydride.



CHIOZZA. *N. Ann. Chim. Phys.* 39, 207; *Ann. Pharm.* 85, 231.

*Acide p  largonique anhydre, P  largonate p  largonique.*

Obtained, similarly to caprylic anhydride, from pelargonate of baryta by means of chlorophosphoric acid.

Colourless oil, lighter than water, solidifying at 0° to a mass of fine needles, which melt at 5°. Smells slightly rancid in the cold, but vinous and aromatic when mixed with hot aqueous vapour.

Chiozza.					
36 C	.....	216	...	72·48	..... 72·4
34 H	.....	34	...	11·41	..... 11·4
6 O	.....	48	...	16·11	..... 16·2
<hr/>					
$\text{C}^{36}\text{H}^{34}\text{O}^6$	.....	298	...	100·00	..... 100·0

Heated on glass, it evolves acrid fumes and the odour of burnt fat. It is very slowly transformed into pelargonic acid by *water*; by aqueous *alkalis* less easily than caprylic anhydride.

### Benzo-pelargonic Anhydride.



CHIOZZA. *N. Ann. Chim. Phys.* 39, 209; *Ann. Pharm.* 85, 231.

*P  largonate de benzoile, Benzoic pelargonate, Pelargonic benzoate.*

Chloride of benzoyl is made to act on pelargonate of baryta; the product is washed with water and dissolved in ether; and the solution decanted from the insoluble part, is shaken with aqueous carbonate of potash.

Colourless oil, resembling anhydrous pelargonic acid, which solidifies to a buttery mass when cooled several degrees below 0°, and immediately liquifies again when warmed. Denser than water.

Chiozza.					
32 C	.....	192	...	73·28	..... 72·9
22 H	.....	22	...	8·40	..... 8·5
6 O	.....	48	...	18·32	..... 18·6
<hr/>					
$\text{C}^{14}\text{H}^5\text{O}^3, \text{C}^{18}\text{H}^{17}\text{O}^3$	...	262	...	100·00	..... 100·0



Evolves slight fumes when heated and is resolved into benzoic and pelargonic anhydrides, products of the decomposition of pelargonic anhydride mixing with them. Exposed over night in single drops to the action of moist air, it becomes filled with needles of benzoic acid.

Easily decomposed by *alkalis*, yielding benzoate and pelargonate of the alkali.

### Pelargone.



CAHOURS. *Chem. Soc. Qu. J.* 3, 240.

Pelargonate of baryta yields by dry distillation, carbonate of baryta and a brown oil which solidifies on cooling. This, when pressed between paper, leaves a solid residue which crystallises from ether in large scales having a pearly lustre.

It is violently acted on by nitric acid and transformed into a nitrogenized acid.

*Oxygen nucleus*  $C^{18}H^{18}O^2$ .

### Anchoic Acid.



G. B. BUCKTON. (1857.) *Chem. Soc. Qu. J.* 10, 166; *J. pr. Chem.* 73, 36; *Lieb. Kopp. Jahrb.* 1857, 303.

C. WIRZ. *Ann. Pharm.* 104, 265.

*Anchoic acid* (Buckton), from ἀνχω, I suffocate. *Lepargylic acid* (Wirz), derived from pelargonic acid by transposition of the letters.

*Formation and Preparation.* 1. *From Chinese-wax.* — When Chinese-wax is heated for several hours with 4 or 5 times its volume of nitric acid of sp. gr. 1.59, the liquid which passes over being poured back, a green-coloured distillate is obtained containing caprylic, œnanthylic, and butyric acid, and a residue from which, after dilution with water, a buttery mass separates. This is filtered off; the acid filtrate is evaporated to crystallisation; and the separated crusts are purified by pressing, melting, washing with ether, and recrystallisation from hot water: anchoic acid then separates, while suberic acid and pimelic acids remain in the mother-liquor. (Buckton.) Cerotic acid treated with nitric acid also yields anchoic acid, but less easily than Chinese-wax. (Buckton.)

2. *From Cocoa-nut-oil.* — The mixture of suberic acid and anchoic acid obtained in the manner described at page 206, is recrystallised till the first separated crystals consist of pure anchoic acid, or such as, on fractional precipitation of its ammonia-salt by nitrate of silver, yields a silver-salt of the composition of anchoate of silver. (Wirz.)

*Properties.* Snow-white, nodular masses. (Buckton.) Round grains, resembling suberic acid but of greater hardness. (Wirz.) Melts at  $114^{\circ}$  —  $116^{\circ}$  (Buckton); at  $115^{\circ}$  in part, at  $124^{\circ}$  completely, and on cooling solidifies to a finely radiated mass having a pearly lustre. (Wirz.) Sublimes, when more strongly heated, with partial decomposition and formation of white, inodorous fumes, which have a suffocating effect when inhaled. (Buckton.) Volatilises partly when its aqueous solution is evaporated. (Wirz.) Tastes but slightly acid. (Buckton.) Has a strong acid reaction. (Wirz.)

	At $100^{\circ}$ .			Buckton.		Wirz.
18 C .....	108	...	57.44	57.02	...	56.6
16 H .....	16	...	8.51	8.68	...	8.6
8 O .....	64	...	34.05	34.30	...	34.8
<hr/>						
$C^{18}H^{16}O^8$ .....	188	...	100.00	100.00	...	100.0

*Combinations. With Water.*—Dissolves in 217.4 parts of water at  $18^{\circ}$ . (Wirz.) Dissolves readily in hot water. The solution becomes white and semifluid on cooling. (Buckton.)

*With Bases.*—Anchoic acid is bibasic, forming both neutral and acid salts.

*Anchoate of Ammonia.*—Amorphous mass, which gives off ammonia when gently heated and is readily soluble in water and alcohol. (Buckton.)

*Anchoate of Potash.*—*a. Neutral.*—Confused crystalline masses, which are very readily soluble in water. (Buckton.)

*b. Acid.*—Microscopic crystalline grains, which do not change at  $140^{\circ}$ . It contains 17.78 p. c. of potassium, agreeing nearly with the formula  $C^{18}H^{16}KO^8$  (calculation 17.25 per cent). It dissolves in 3 parts of cold water, much more readily in hot water. Soluble in wood-spirit. (Buckton.)

*Anchoate of Soda.*—Crystallises more readily than the potash-salt. (Buckton.)

*Anchoate of Baryta.*—*Neutral.*—Obtained by neutralising the acid with baryta-water (Buckton), or by precipitating a mixture of anchoate of ammonia and chloride of barium with alcohol (Wirz); in the latter case as a jelly. Or by neutralising anchoic acid with moist carbonate of baryta and evaporating. (Wirz.)

Transparent pellicle, opaque at  $100^{\circ}$ . (Buckton.) After drying over oil of vitriol, it forms a white, opaque, porcelain-like mass. (Wirz.) It is very readily soluble in water, insoluble in alcohol and ether. (Buckton.)

				Wirz.	Buckton.
$C^{18}H^{14}O^8$ .....	186	...	57.6		
2 Ba .....	137	...	42.4	42.24	42.40
<hr/>					
$C^{18}Ba^2H^{14}O^8$ .....	323	...	100.0		

Acid anchoate of baryta cannot be obtained. (Buckton.)

Anchoate of ammonia forms with *chloride of calcium*, a gelatinous precipitate; with *acetate of lead*, white; with *protosulphate of iron*, whitish. With *sesquichloride of iron*, bright brick-red; and with *sulphate of copper*, bluish green. (Wirz.) It also precipitates the salts of *zinc*, and *mercurous* and *mercuric* salts. (Buckton.)

*Anchoate of Silver. — Neutral.* — Obtained from the ammonia-salt by double decomposition, as a white powder, changing readily when moist, (Wirz). White flakes which do not change at  $120^\circ$ , and are but slightly soluble in water. (Buckton.)

	At $100^\circ$ .			Wirz.	Buckton.
18 C .....	108	...	26.8	.....	26.35
14 H .....	14	...	3.4	.....	3.45
2 Ag.....	216	...	58.7	.....	53.75
8 O .....	64	...	16.1	.....	16.45
<hr/>					
$C^{18}H^{14}Ag^2O^8$ ....	402	...	100.0	.....	100.00

### Anchoate of Ethyl.



BUCKTON. *Chem. Soc. Qu. J.* 10, 166; *J. pr. Chem.* 73, 38.

WIRZ. *Ann. Pharm.* 104, 268.

Obtained by passing hydrochloric acid into an alcoholic solution of anchoic acid. (Buckton, Wirz.)

Yellowish (Wirz) semi-fluid oil. (Buckton.) Lighter than water. Has an agreeable odour (Buckton); slightly resembling that of rennet-apples. (Wirz.) Boils above  $325^\circ$ . (Buckton.) Becomes brown at  $260^\circ$  without distilling. (Wirz.) Is insoluble in water. (Buckton.)

				Wirz.
26 C .....	156	...	63.9	..... 63.7
24 H .....	24	...	9.8	..... 9.9
8 O .....	64	...	26.3	..... 26.4
<hr/>				
$2C^4H^6O, C^{18}H^{14}O^6$ ....	244	...	100.0	..... 100.0

### Oxygen-nucleus $C^{18}H^{14}O^4$ .

### Crotonol. $C^{18}H^{14}O^4$ .

TH. SCHLIPPE. *Ann. Pharm.* 105, 1; *Chem. Centr.* 1858, 279; *J. pr. Chem.* 73, 279.

*Sources.* In the oil obtained by pressing the seeds of *Croton tiglium*.

*Preparation.* Croton-oil is shaken with a sufficient quantity of alcoholic soda to produce a milk; the liquid is gently heated for several hours; and water or a solution of common salt is added, whereupon a

layer of oil forms on the surface, which is completely removed by repeated filtration through wet filters. The filtrate yields, on addition of hydrochloric acid, another oil, which is digested with hydrated oxide of lead till the acid reaction ceases (whereby a flocculent precipitate is formed, which becomes smeary and adhesive), and then mixed with soda and a large quantity of water. The milky fluid thus formed, becomes clear by depositing an oil, which is washed with water, first by itself and then after solution in ether. The ethereal solution evaporated in vacuo leaves crotonol, amounting to 4 p. c. of the croton-oil.

*Properties.* Colourless or faintly wine-yellow, tough, turpentine-like mass, having a faint odour. It is the constituent of the croton seed which irritates the skin, not that which purges.

It cannot be distilled.

					Schlippe. mean.
18 C	.....	108	....	70.13	..... 69.84
14 H	.....	14	....	9.09	..... 9.35
4 O	.....	32	....	20.78	..... 20.81
<hr/>					
$C^{18}H^{14}O^4$	....	154	....	100.00	..... 100.00

*Decompositions.* 1. When heated in vacuo (at 50 mm. pressure) it blackens, but does not distil. On heating crotonol in a stream of carbonic acid to  $130^{\circ}$ — $150^{\circ}$ , but little water passes over; the residual portion is less acrid than crotonol. — 2. Crotonol is decomposed by heating, evolving mild fumes. — 3. When distilled with water, either pure or containing sulphuric acid, it yields an oil (mould-oil) which passes over, colourless at first but afterwards black; floats on the distillate; cannot be distilled by itself, even in vacuo at  $200^{\circ}$ ; and has a very nauseous and mouldy smell, and leaves a black resin which gives with alcohol a turbid solution precipitable by basic acetate of lead. — 4. Dissolved in absolute alcohol and cooled, it does not yield crystals when ammonia is passed into it. — 5. Does not combine with concentrated bisulphite of soda. — With melting sodium, it violently evolves gases and becomes still more viscid and resinous, so that the action of the sodium soon abates. — 7. By boiling with a solution of potash, or soda, it is converted into a brown resin which no longer reddens the skin.

Alcoholic crotonol does not precipitate metallic salts.

*Chlorine-nucleus*  $C^{18}ClH^{17}$ .

**Chloride of Pelargyl.**

$C^{18}ClH^{17}O^2 = C^{18}H^{17}Cl, O^2$ .

CAHOURS, *Chem. Soc. Qu. J.* 3, 240; *Compt. rend.* 39, 257.

*Chlorure de p  largyle, Chlorpelargyl.*

*Formation.* (p. 369). The mixture of chlorophosphoric acid and chloride of pelargyl which passes over in the action of pentachloride of phosphorus on pelargonic acid is separated by repeated distillation and removal of the first portion of the distillate, till the boiling point becomes constant.

Colourless liquid, which boils at  $220^{\circ}$ . Denser than water. Has a powerful odour. Emits strong fumes in the air. Becomes heated when mixed with alcohol and forms pelargonic ether. By hydrated oxide of phenyl it is converted, with evolution of hydrochloric acid, into a volatile liquid, which, by boiling potash, is resolved into hydrated oxide of phenyl and pelargonic acid:



*Nitrogen-nucleus*  $C^{18}N^2H^{18}$ .

### Acetonine.



STÄDELER. *Gött. Nachrichten* 1853, 121; *Pharm. Centr.* 1853, 433; *N. Ann. Chim. Phys.* 42, 226; more fully, *Ann. Pharm.* 111, 308.

*Formation.* 1. The solution of ammonia in acetone leaves by spontaneous evaporation, a colourless syrup, which in time changes into acetonine.—2. This compound is likewise formed when acetone saturated ammonia is heated to  $100^{\circ}$  in a sealed glass tube.

*Properties.* Colourless liquid, having a peculiar urinous odour, and a burning taste and alkaline reaction.

Readily soluble in water. The aqueous solution becomes turbid for a while when heated. Potash separates acetonine from it in oily drops.

*Chloroplatinate of Acetonine.* —  $C^{18}H^{18}N^2, HCl, PtCl^2$  Lustrous, orange-coloured four-sided prisms with oblique terminal faces. Soluble in water and in boiling alcohol containing hydrochloric acid. Insoluble in ether. Gives by analysis 27.96 p. c. platinum, the formula requiring 27.37 p. c.

*Oxalate of Acetonine.* —  $C^{18}H^{18}N^2, C^4H^2O^8 + 2Aq$ . Crystallises from the hot saturated alcoholic solution in delicate colourless prisms, which lose 2 At. of water at  $100^{\circ}$ , are decomposed at a higher temperature, are readily soluble in water, but insoluble in ether. The crystals give by analysis 50.00 p. c. carbon, and 8.41 hydrogen, the formula requiring 50.38 C, and 8.40 H. They give off 3.43 p. c. (1 At.) water at  $100^{\circ}$ .

Acetonine is readily soluble in *alcohol* and in *ether*.

Fittig (*Ann. Pharm.* 110, 17) could not, in a great number of experiments, obtain acetonine by the method above given, but by spontaneous evaporation of the acetone which had been saturated with ammonia and heated in the water-bath, he obtained crystals of paracetone with 6 At. water ( $C^6H^6O^2 + 6Aq$ ). Städeler, however (*Ann. Pharm.* 100, 300), maintains his former statements, and attributes Fittig's results to errors of experiment (see additions to vol. ix, at the end of this volume).

### Thiacetonine. $C^{18}H^{19}NS^4$ .

STÄDELER. *loc. cit.* (compare ix, 14).

Produced by the action of ammonia and sulphuretted hydrogen on acetone:



Acetone is treated with ammonia and sulphuretted hydrogen alternately, till an oily liquid is obtained, floating on a crystalline pulp of sulphhydrate of ammonia. This liquid, which has an extremely fetid odour, is sometimes merely a mixture of oily basic products, but sometimes it contains also a crystallizable base, which is thiacetone. — To separate this base the crude oil is digested with ether; hydrochloric acid is added by drops, and the resulting solid product is freed from an adhering syrupy liquid by washing with ether, solution in water, evaporation to dryness, and washing with alcohol. Hydrochlorate of thiacetone is thus obtained from which the base itself may be precipitated by ammonia.

Thiacetone appears also to be produced by the dry distillation of sulphhydrate of carbothiacetone;



or by boiling the alcoholic solution of that substance :



Thiacetone has a very faintly sweet and, at the same time, rather bitter taste; its odour is not peculiarly repulsive. It dissolves readily in alcohol and ether, and may be obtained in good crystals from the alcoholic, and likewise from the ethereal solution, if the latter be poured upon water in a tall vessel and the ether left to evaporate. The crystals, heated in a glass tube, melt and sublime completely in colourless oil-drops which partly solidify in the crystalline form on cooling. Heated with soda-lime, it gives off ammonia in large quantity, and yields oily drops which smell like chinoline and solidify after a short time in the crystalline form. Heated with nitre and hydrate of potash, it forms a saline mass, rich in sulphuric acid.

Thiacetone dissolves without decomposition in hydrochloric, nitric, sulphuric, and acetic acid, forming crystalline salts. — The *hydrochlorate* crystallizes from its aqueous solution by spontaneous evaporation in beautiful nacreous plates, having angles of  $78^\circ$  and  $102^\circ$  nearly. It dissolves readily in water, much less in cold alcohol, very easily in boiling alcohol, not at all in ether. Has a faint odour and a peculiar sweet and bitterish taste. The solutions are neutral. Heated in a glass tube, it sublimates, leaving a little charcoal and forming oily drops which gradually crystallize. Nitrate of silver added to its solution throws down chloride of silver; but on heating, especially if ammonia has been added, sulphide of silver is formed. — The original hydrochlorate of thiacetone (*vid. sup.*), gave by analysis 19 p. c. and 16.93 p. c. hydrochloric acid, whereas the formula  $\text{C}^{16}\text{H}^{10}\text{NS}^4, \text{HCl}$  requires 15.11 p. c. Probably it contained sal-ammoniac; moreover both determinations were made with only 0.1 grm. of substance. — *Chloroplatinate of thiacetone* is a lemon-yellow crystalline precipitate. — The *nitrate* forms long colourless four-sided prisms with oblique terminal faces, sparingly soluble in water and alcohol. — The *sulphate*, which crystallizes with difficulty, is sparingly soluble in water, insoluble in alcohol. — The *acetate* is very soluble in water and alcohol, and difficult to crystallize. — The *chromate*, obtained by mixing the solution of the hydrochlorate with chromate of potash, is a thick yellow flocculent precipitate which gradually becomes crystalline.

Thiacetone is probably identical with Zeise's *alcethine* (ix, 12).

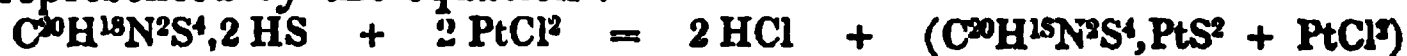
**Carbothiacetone.  $C^{20}H^{18}N^2S^4$ .**

STÄDELER. *loc. cit.*—Further, *Ann. Pharm.* 111, 316.

Produced, as a sulphydrate, by the action of aqueous ammonia and bisulphide of carbon (*i. e.* of sulphocarbonate of ammonium) on acetone :



The sulphydrate of carbothiacetone thus produced is a crystalline body [originally obtained by Hlasiwetz [ix, 14], who however assigned to it the improbable formula  $2C^6H^6S, C^2H^2NS^2 + 2(C^6H^6, C^2NS^2) = C^{20}H^{26}N^2S^9$ ], which, gives by analysis 45.54 p. c. carbon, 7.13 hydrogen, 10.69 nitrogen, and 37.23 sulphur, agreeing nearly with the formula  $C^{20}H^{20}N^2S^6$ , which requires 45.46 C, 7.58 H, 10.61 N, and 36.35 S. — Its alcoholic solution mixed with bichloride of platinum yields a brownish yellow amorphous precipitate, which may be dried at  $100^\circ$ , without decomposition, and then yields by analysis 22.84 p. c. C, 3.32 H, 5.48 N, and 37.64 Pt., represented, according to Städeler, by the formula  $C^{20}H^{18}N^2S^4, PtS^2 + PtCl^2$ , requiring 22.63 C, 3.40 H, 5.28 N, and 37.19 Pt. Its formation may be represented by the equation :



Hlasiwetz assigned to this precipitate the formula  $C^{20}H^{26}N^2S^9, 3 PtS^2$ .

*Primary Nucleus  $C^{18}H^{20}$ .**Oxysulphi-nucleus  $C^{18}(SO^2)^2H^{16}O^2$ .***Sulphocamphoric Acid.**

PH. WALTER. (1840.) *Ann. Chim. Phys.* 74, 38; *J. pr. Chem.* 21, 241; *Ann. Pharm.* 36, 59; *N. Ann. Chim. Phys.* 9, 177.

*Acide sulfocamphorique, Campherschwefelsäure.*

*Formation.* By the action of anhydrous, fuming, or common sulphuric acid on camphoric acid.

*Preparation.* Finely powdered camphoric acid is introduced in small portions into a platinum capsule half filled with oil of vitriol, so that the oil of vitriol remains in great excess, whereby the camphoric acid is dissolved to a perfectly limpid liquid. When either fuming or anhydrous sulphuric acid is used, sulphurous acid is evolved, and the fluid becomes yellow or brown and afterwards darker. On carefully heating the solution, bubbles of carbonic acid are evolved from  $45^\circ$  to  $50^\circ$ , more abundantly at  $60^\circ$ , so that to prevent overflowing, the basin must be frequently removed from the water-bath. The liquid is stirred, and the heating continued as long as carbonic acid is evolved, and the now brown liquid is diluted with a large



quantity of water and allowed to stand for several days, whereupon the undecomposed camphoric acid is deposited, together with a green substance which colours the aqueous mixture green. The liquid is filtered and evaporated to crystallisation in vacuo over sulphuric acid, which is frequently renewed; the crystals are drained on a funnel, repeatedly pressed between blotting paper, afterwards ground and again pressed to remove the adhering sulphuric acid as much as possible, then dissolved in alcohol, and the solution is allowed to evaporate spontaneously. The crystals obtained are collected, pressed, and again recrystallised from alcohol, until they are nearly colourless, then once more crystallised from water and allowed to dry in the air on blotting paper. Formerly Walter decomposed the mixture of sulphocamphoric acid and oil of vitriol with carbonate of baryta or oxide of lead, then the baryta-salt with sulphuric acid, or the lead-salt with sulphuretted hydrogen; but in this manner he never obtained the acid dry or of constant composition, but contaminated with sulphuric acid, as the lead-salt is accompanied by a product of decomposition containing sulphuric acid. This sulphuric acid Walter formerly erroneously supposed to be derived from the sulphocamphoric acid by its decomposition in the evaporation of its aqueous solution.

*Properties.* Hydrated sulphocamphoric acid forms colourless, six-sided prisms. It has a very sour taste, and makes the teeth feel blunt. In vacuo the crystals lose 4 At. of water = 12.5 p. c. (Calculation 12.49 p. c.), and also their crystalline structure, passing into anhydrous sulphocamphoric acid, which likewise remains on evaporating the aqueous solution to dryness in the water-bath.

<i>Dried in vacuo.</i>				Walter.
18 C	108	...	42.82	43.01
16 H	16	...	6.34	6.42
12 O	96	...	38.09	37.79
2 S	32	...	12.75	12.78
<hr/>				
$C^{18}H^{16}S^2O^{12}$	252	...	100.00	100.00
<hr/>				
<i>Crystallised.</i>				Walter.
18 C	108	...	37.47	37.82
20 H	20	...	6.94	7.02
16 O	128	...	44.43	43.95
2 S	32	...	11.16	11.21
<hr/>				
$C^{18}H^{16}S^2O^{12} + 4Aq$	288	...	100.00	100.00

*Decompositions.* 1. The acid gives off water of crystallisation when heated on platinum-foil, melts (on mercury at 160° to 165°) undergoing decomposition, acquires a red colour, then chars, evolves thick white fumes, and entirely disappears. — 2. The aqueous solution may be evaporated to dryness in the water-bath without undergoing decomposition. — 3. It is but sparingly soluble in cold oil of vitriol, more soluble on the application of heat; but when strongly heated, the solution acquires a red, then becomes black, the colour being already very dark when near the boiling point—the sulphocamphoric acid being destroyed and sulphurous acid evolved. With anhydrous sulphuric acid, it forms a blood-red solution, with partial decomposition. — 4. It is not changed by trituration with iodine. — 5. With bromine, it evolves hydrobromic acid gas, and yields a compound denser than water. — 6. When chlorine is



passed through aqueous sulphocamphoric acid, a viscid oil separates, sinking to the bottom; this oil burns with a greenish flame when heated.

*Combinations.* Sulphocamphoric acid is very readily soluble in *water*; single scales dissolve almost instantaneously, moving rapidly to and fro; the anhydrous acid dissolves even more quickly and with more rapid movements.

Soluble in *hydrochloric*, *nitric* and cold *sulphuric acid*, without decomposition.

Insoluble in bisulphide of carbon.

Sulphocamphoric acid is bibasic. All its salts are soluble. Only *neutral* salts  $= C^{18}H^{14}M^2S^2O^{12}$  are known.

*Sulphocamphorate of Ammonia.* — Concentrated aqueous sulphocamphoric acid is supersaturated with ammonia, and the mixture allowed to evaporate spontaneously in the air (in vacuo nearly all the ammonia escapes). This salt has a somewhat variable composition, owing to the tendency of the ammonia to escape.

Needles grouped in stars, having an acrid, pungent taste. Reddens litmus. Very soluble in water, somewhat soluble in alcohol.

						Walter.
18 C	.....	108	...	35.52	.....	35.5
2 N	.....	28	...	9.21	.....	9.4
24 H	.....	24	...	7.89	.....	7.7
2 S	.....	32	...	10.52	.....	10.5
14 O	.....	112	...	36.86	.....	36.9
$C^{18}H^{14}(NH^4)^2S^2O^{12} + 2Aq$ .....						304 ... 100.00 ..... 100.0

*Sulphocamphorate of Potash.* — (When aqueous sulphocamphoric acid is neutralised with potash and left to evaporate, a salt which reddens litmus crystallises on the upper part of the vessel in masses resembling cauliflower-heads, and at the bottom of the vessel a salt composed of needles and producing a brown stain on turmeric paper). Sulphocamphoric acid dissolved in absolute alcohol is neutralised with alcoholic potash, whereupon the salt separates in fine needles as soon as the neutralisation is nearly complete, so that the liquid solidifies. The product is collected on a filter, washed with alcohol, pressed and then dried, first in the air, then in vacuo.

Very slender, colourless needles. Taste acrid, cooling, similar to that of Epsom salts. Neutral to vegetable colours. Dissolves rapidly in water with movements similar to those of sulphocamphoric acid. Sparingly soluble in alcohol, still less in absolute alcohol, very sparingly in ether.

						Walter.
2 KO	.....	94.4	...	28.74	.....	28.65
18 C	.....	108	...	32.88	.....	32.65
14 H	.....	14	...	4.26	.....	4.35
10 O	.....	80	...	24.36	.....	24.48
2 S	.....	32	...	9.76	.....	9.87
$C^{18}H^{14}K^2S^2O^{12}$ .....						328.4 ... 100.00 ..... 100.00

*Sulphocamphorate of Baryta.* — The aqueous acid is saturated with carbonate of baryta, the saturation being promoted by the aid of heat.

The filtered solution leaves on evaporation a colourless, or slightly yellow, gummy, non-crystalline mass, easily detached. (When the mixture of sulphuric acid and sulphocamphoric acid, diluted with a large quantity of water is neutralised with carbonate of baryta, a yellowish, impure salt is obtained, other products of decomposition being mixed with it.)

Tastes unpleasant, very saline and at the same time sweet. Reddens litmus slightly. Burns when heated on platinum-foil, and leaves a greenish white mass, which is a mixture of sulphide of barium and sulphate of baryta.

					Walter.
2 BaO .....	153	...	39.53	.....	39.50
18 C .....	108	...	27.88	.....	28.40
14 H .....	14	...	3.61	.....	3.63
10 O .....	80	...	20.68	.....	20.18
2 S .....	32	...	8.30	.....	8.29
<hr/>					
$C^{18}H^{14}Ba^2S^2O^{12}$ .....	387	...	100.00	.....	100.00

*Sulphocamphorate of Lime.* — Aqueous sulphocamphoric acid is neutralised with lime-water and the solution evaporated in vacuo over oil of vitriol, a non-crystalline residue remaining.

Soluble in water, less soluble in alcohol.

					Walter.
2 CaO ... ..	56	...	19.31	.....	19.2
18 C .....	108	...	37.24	.....	34.6
14 H .....	14	...	4.82	.....	5.0
10 O .....	80	...	27.59	.....	30.3
2 S .....	32	...	11.04	.....	10.9
<hr/>					
$C^{18}H^{14}Ca^2S^2O^{12}$ .....	290	...	100.00	.....	100.0

*Sulphocamphorate of Lead.* — Prepared like the baryta-salt. The solution evaporated over the water-bath, in vacuo, or spontaneously, leaves an amorphous mass, which yields a white powder when ground. Tastes sweet, like other lead-salts. Reddens litmus. When heated on platinum foil it burns and leaves oxide of lead. Soluble in water, insoluble in alcohol.

<i>Dried in vacuo or at 120°–130°.</i>					Walter.
2 PbO .....	223.6	...	48.64	.....	48.84
18 C .....	108	...	23.62	.....	23.63
14 H .....	14	...	3.07	.....	3.08
10 O .....	80	...	17.64	.....	17.37
2 S .....	32	...	7.03	.....	7.08
<hr/>					
$C^{18}H^{14}Pb^2S^2O^{12}$ ...	457.6	...	100.00	.....	100.00

*Sulphocamphorate of Copper.* — When aqueous sulphocamphoric acid is neutralised with oxide or carbonate of copper, and the green solution left to evaporate, nodular crystals are obtained, which seem to be  $C^{18}H^{14}Cu^2S^2O^{12} + 2Aq$ ; it is however difficult to obtain the salt pure, and it is generally contaminated with an acid salt, which can be extracted by repeated washing with alcohol.

*Sulphocamphorate of Baryta and Copper.* — When sulphate of copper is added in small quantities to cold aqueous sulphocamphorate of baryta

until no more sulphate of baryta is precipitated, and the green filtrate is evaporated over the water-bath, sulphate of baryta is continuously precipitated, and at last a solution free from baryta remains, which crystallises on evaporation. In vacuo, at the common temperature, the green filtrate may be evaporated without undergoing decomposition. Accordingly a double salt first forms in the cold, which deposits sulphate of baryta when heated. As the sulphuric acid can form only at the expense of the oxygen in the organic substance (or the oxide of copper), the crystallised salt must contain a modified sulphocamphoric acid.

*Sulphocamphorate of Silver.* — When aqueous sulphocamphoric acid is neutralised with oxide of silver, the filtered solution evaporated in the water-bath or in vacuo, deposits crystalline crusts ; but it often becomes yellow, and then yields a salt having a faint yellow colour.

Sometimes colourless, sometimes yellow crystalline crusts, having a very disagreeable and strongly metallic taste. Reddens litmus. Less soluble in water than the sulphocamphorates above described. Sparingly soluble in cold alcohol, more soluble in hot alcohol.

					Walter.
2 Ag	.....	216.2	...	46.37	..... 46.38
18 C	.....	108	...	23.18	..... 23.02
14 H	.....	14	...	3.00	..... 2.99
12 O	.....	96	...	20.59	..... 20.72
2 S	.....	32	...	6.86	..... 6.89
<hr/>					
$C^{18}H^{14}Ag^2S^2O^{12}$	...	466.2	...	100.00	..... 100.00

Sulphocamphoric acid dissolves very readily in common and in absolute *alcohol*.

It is soluble in *ether*.

It is insoluble in cold, and very sparingly soluble in hot *oil of turpentine*.

## ADDITIONS TO VOL. VII.

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Page 133.

*Action of Potash and Soda on Organic Compounds.* — The action of these two alkalis on organic substances is not always the same, the use of potash being more advantageous than that of soda, for the production of certain compounds. The two following instances of the difference of action have been particularly examined by Possoz. (*N. Ann. Chim. Phys.*, 56, 301):

1. *Formation of Oxalates.* When starch, sawdust, straw, bran, wool, silk, leather, horn, &c., is heated with strong potash-ley to a temperature between  $200^{\circ}$  and  $225^{\circ}$ , the solid matter dissolves and forms a brown mass containing a considerable quantity of ulmic acid; and on continuing the heat, the mass becomes yellow and whitish, and the ulmic acid is converted into oxalic acid, together with acetic and formic acids. With 300 pts. of hydrate of potash to 100 pts. of organic matter dried at  $100^{\circ}$ , starch yields 125 pts. of oxalic acid; sawdust, 70; straw, 100; hay, 140; bran, 150; wool, 10; silk, 12; leather, 6; horn, 20.

When soda is used instead of potash, ulmic acid is first produced as above; but when the heat is continued, the oxalic, acetic, and formic acids appear to be decomposed nearly as fast as they are formed; their presence may indeed be recognised during the whole course of the action; but at whatever point the operation may be stopped, or whatever proportion of soda may be used, the quantity of oxalic acid obtained is always very small—and sometimes, as in the case of wool, silk or leather, absolutely nothing.

This destructive action of soda appears to be due to the comparatively high temperature at which it melts; even when potash is used, the product is much diminished if the heat is allowed to rise too high. But when the hydrates of soda and potash are mixed in such proportion that the mass shall fuse at nearly the same temperature as pure potash, the quantity of oxalic acid produced is the same as when potash alone is used, or may even be greater. The addition of soda in certain proportions renders it possible to operate on a larger quantity of organic matter, and the quantity of oxalic acid produced increases in the same proportion. A mixture of 1 pt. of hydrate of soda with 3 pts. hydrate of potash decomposes  $\frac{1}{10}$  more starch than pure potash; 1 pt. of soda with 2 pts. potash, decomposes  $\frac{1}{8}$  more; a mixture of the two alkalis in equal parts decomposes about the same quantity as pure potash; a mixture 2 pts. soda and 1 potash decomposes  $\frac{1}{10}$  less; 3 pts. soda with 1 pt. potash,  $\frac{1}{8}$  less; and with a still larger proportion, the quantity of oxalic acid produced is very small.

2. *Formation of Cyanides.* Soda, either pure or carbonated cannot be used to replace potash in the manufacture of ferrocyanides (vii. 453). If used alone, it yields a much smaller product; and the addition of soda to the potash diminishes instead of increasing the quantity of cyanide formed. The cause of this difference appears to be that the deoxidation of soda by carbon requires a higher temperature than that of potash; and in consequence of this higher temperature, the animal matter is decomposed and gives off its nitrogen in the gaseous form, before the sodium is set free and enabled to unite with the carbon and nitrogen. In preparing cyanides by passing nitrogen gas over charcoal impregnated with an alkaline carbonate, it is found that when carbonate of soda is used, a much higher temperature is required than with potash. (Possoz.)

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Page 170.

*Alcohol-radicals, &c. from Boghead Cannel Coal.* — The light oil (A) obtained by distilling Boghead Cannel coal at a gentle heat, contains *alcohol-radicals*  $C^{2n}H^{2n+2}$  or  $(C^nH^{n+1})^2$ ; hydrocarbons  $C^{2n}H^{2n}$  homologous with olefiant gas; and hydrocarbons  $C^{2n}H^{2n-6}$  homologous with benzol.

1. The oil has a specific gravity of 0.750 at 15°, and begins to boil at 141°. By treating it with fuming nitric acid or with a mixture of nitric and sulphuric acids, separating that portion of the oily liquid which is not altered by the action of the acid, washing it with aqueous alkali, drying it by contact with a solid alkaline hydrate, rectifying over sodium, and repeated fractional distillation, the following alcohol-radicals are obtained.

Name.	Formula.	Boiling point.	Sp. gr. at 18°.	Vapour-density.	
				exp.	calc. (2 vol.)
Propyl or Trityl ....	$(C^3H^7)^2$	68°	0.6745	2.96	2.97
Butyl or Tetryl ....	$(C^4H^9)^2$	119°	0.6945	3.88	3.94
Amyl or Pentyl ....	$(C^5H^{11})^2$	159°	0.7365	4.93	4.91
Caproyl or Hexyl ....	$(C^6H^{13})^2$	202°	0.7568	5.83	5.87

2. The original oily distillate (A) treated with bromine in presence of water is converted into a heavy liquid which is a mixture of the bromides of the hydrocarbons  $C^{2n}H^{2n}$  with the hydrocarbons  $C^{2n}H^{2n+2}$  and  $C^{2n}H^{2n-6}$ . These latter hydrocarbons may be separated by distillation (B), the bromides  $C^{2n}H^{2n}Br^2$  then remaining behind. The brominated product being formed in presence of water, could not be obtained free from oxygen. After standing for some time, it separated into three layers, the upper consisting of water, with a small quantity of hydro-

bromic acid, the middle layer of organic bromine-compounds (C); the lowest of aqueous hydrobromic acid (of sp. gr. 1.320, containing 37 p. c. HBr).

The organic bromine-compounds (C) when repeatedly treated with alcoholic solution of potash and sodium, reproduced the hydrocarbons from which they had been formed. The brominated oil formed from the portion of the original oil which boiled between  $71^{\circ}$  and  $72^{\circ}$ , yielded *caproylene* (*hexylene*)  $C^{12}H^{12}$  (vapour-density observed: 3.020; calc. 2.904); and the brominated oil from the portion boiling between  $82^{\circ}$  and  $88^{\circ}$ , yielded *œnanthylene* (*heptylene*)  $C^{14}H^{14}$  (sp. gr. 0.718 at  $18^{\circ}$ . Vapour-density, observed: 3.320; calc. 3.386).

3. By treating the mixture of hydrocarbons (B) distilled from the bromides, with fuming nitric acid, *benzol* is dissolved as nitrobenzol, the alcohol-radicals  $C^{2n}H^{2n+2}$  remaining unaltered. A small quantity of toluol appears to be likewise present, but no other hydrocarbon of the same series. (C. G. Williams, *Phil. Trans.* 1857, 447; abstr. *Phil. Mag.* [4], 13, 134; *Chem. Gaz.* 1857, 19 and 25; *Ann. Pharm.* 102, 126. Further; *Phil. Trans.* 1857, 737; *Chem. Gaz.* 1858, 285; abstr. *Ann. Pharm.* 108, 384.)

Page 175.

*Volatile Organic Bases* (natural occurrence). — According to O. Hesse (*J. pr. Chem.* 70, 60) *guano* contains traces of amylamine and trimethylamine. Both these bases, especially the latter, are likewise found in the leaves of *mangold-wurzel*. According to Lucius (*Ann. Pharm.* 103, 105) *guano* likewise contains bimethylamine, 28 lbs. of *guano* distilled with lime yielding 0.5 grm. of a platinum-salt agreeing in composition with the formula  $C^4H^7N \cdot HCl \cdot PtCl^2$ .

Putrid *yeast* contains, according to A. Müller's investigation (*J. pr. Chem.* 70, 65) trimethylamine and amylamine, probably also ethylamine and caprylamine. — According to Hesse (*J. pr. Chem.* 71, 471), the volatile bases produced by the putrefaction of yeast are trimethylamine, ethylamine, amylamine, and perhaps also caprylamine.

Page 202.

*Fatty Acids*. — According to Perrott (*Compt. rend.* 45, 174), fusel-oil obtained from beet contains several acids of the series  $C^{2n}H^{2n}O^4$ , viz. valerianic, caproic, œnanthylic, caprylic, and pelargonic acids. the two latter being the most abundant. These acids exist in the fusel-oil in the form of ethers, and may be separated as potash-salts by treating with potash the residue which remains after distilling off the amylic alcohol.

Formic, acetic, propionic and butyric acids have been found among the product of the dry distillation of Irish peat. (Sullivan, *Atlantis*, 1, 185.)

— Acetic, butyric, and valerianic acids have also been found among the products of the distillation of a light moss-peat from the Canton Zurich. (Vohl, *Ann. Pharm.* 109, 152.) Kraut found caproic and butyric acids in the residue obtained by evaporating 25 litres of the water of a spring rising in boggy ground in Hanover, after the water had stood for some months in a vessel half filled with it. The fresh water exhibited scarcely any trace of those acids. (*Ann. Pharm.* 103, 29.)

Lucius (*Ann. Pharm.* 103, 105) found in guano a large quantity of acetic acid, a smaller quantity of propionic, and very little formic acid. According to Rebling (*Arch. Pharm.* [2] 92, 82) butyric acid is present as an odoriferous principle in guano and in human fæces; also in the excrements of carnivorous birds, and of serpents (*ibid.* 93, 300).

Al. Müller (*J. pr. Chem.* 70, 65) found in putrid yeast, large quantities of acetic, butyric, caprylic and butyro-acetic acids, very little formic and pelargonic acids, and an acid containing more than 20 At. carbon; Hesse (*J. pr. Chem.* 71, 471) found in putrefied yeast, acetic, butyric and propionic acids, probably also formic, caprylic and pelargonic acid.

### Page 215.

*Action of Alkaline Hydrates on Compound Ethers.* — Compound ethers decomposed by alkalis generally yield alcohols; sometimes, however, especially with nitric ethers, the product of the decomposition is not an alcohol but a simple ether, just as in the precipitation of metallic salts by potash, the precipitate is sometimes an anhydrous oxide instead of a hydrate.

When *nitrate of methyl* is introduced into an inverted glass tube standing over mercury, and a piece of solid potash is passed up together with a little water, a formation of gas begins in two or three days, and continues for some weeks. The gas thus evolved is oxide of methyl:



The quantity of methylic ether thus obtained is about  $\frac{1}{2}$  of the theoretical quantity; the rest of the methyl is probably converted into methylic alcohol.

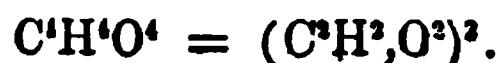
*Nitrate of ethyl* heated with solid potash, yields a mixture of alcohol and ether, together with a considerable quantity of brown humus-like matter. With dilute potash-solution, nothing but alcohol is obtained.

Sulphide of ethyl under the same circumstances yields nothing but alcohol.

Bromide of ethyl treated with hydrate of potash sometimes yields ether. (Borthelot, *Compt. rend.* 49, 212.)

Page 246.

# Bioxymethylene.



A. BUTLEROW. *Ann. Pharm.* 111, 242 ; *Compt. rend.* 49, 137.

## Dioxymethylene.

*Formation.* 1. By the action of oxalate of silver on iodide of methylene :



2. By the action of oxide of silver on iodide of methylene. — 3. By the action of oxide of lead on acetate of methylene (p. 392).

*Preparation.* When 1 At. iodide of methylene is intimately mixed with 1 At. oxalate of silver, and heated, a violent explosive action takes place; but if the mixture be previously triturated with twice its weight of pounded glass, — or better, if it be heated under a layer of rock-oil, a slow regular decomposition takes place; gas is abundantly evolved consisting of carbonic acid and carbonic oxide; and bioxymethylene sublimes in the neck of the retort or passes over with the vapour of rock-oil into the receiver, and there condenses in a thin white layer, which adheres closely to the sides of the receiver. It is purified by pressure between paper, and washing with ether, alcohol and water, then with alcohol and ether, in the order here mentioned, and lastly dried over oil of vitriol and sublimed in sealed tubes.

*Properties.* Translucent, hard, crystalline crusts having an indistinct crystalline structure. It is odourless at ordinary temperatures, but emits a peculiar, sharp, irritating odour when heated. Tasteless. Neutral to litmus paper. May be sublimed without previous fusion. Begins to volatilize at 100°, but is not completely vaporized till heated above 150°; at about 152°, it melts and immediately afterwards begins to boil. A lump of it quickly heated, melts and boils at the same time. Vapour-density 2·07.

Butlerow.						Vol.	Density.
4 C	24	...	40·00	.....	39·08	.....	C-vapour..... 4 .... 1·6640
4 H	4	...	6·67	.....	6·78	.....	H-gas ..... 4 .... 0·2772
4 O	32	...	53·33	.....	54·14	.....	O-gas ..... 2 .... 2·2186
<hr/>							
C <sup>4</sup> H <sup>4</sup> O <sup>4</sup>	...	60	...	100·00	.....	100·00	..... Vap. of C <sup>4</sup> H <sup>4</sup> O <sup>4</sup> .... 2 .... 4·1598
							1 .... 2·0799

Isomeric with acetic acid and formiate of methyl. It might also be regarded as methyl-glycolic ether  $\left. \begin{matrix} C^2H^2 \\ C^2H^2 \end{matrix} \right\} O^4$ , were it not that Wurtz's recent investigations seem to show that the ethers of biatomic alcohols contain the same number of carbon-atoms as the alcohols themselves ; and consequently that methyl-glycol (not yet obtained) being  $\left. \begin{matrix} C^2H^2 \\ H^2 \end{matrix} \right\} O^4$ , methyl-glycolic ether should be C<sup>2</sup>H<sup>2</sup>O<sup>2</sup>.



**Decompositions.** 1. Bioxymethylene has a great inclination to take up an additional quantity of *oxygen*, being thereby converted into carbonic acid and water, and sometimes partially into formic and oxalic acids. It reduces the oxides of silver and mercury when heated with them. *Nitric acid* or a mixture of *sulphuric acid* and *bichromate of potash* converts it into carbonic acid and water. Enclosed, together with *spongy platinum*, in a sealed tube containing oxygen, it oxidises slowly at ordinary, quickly at higher temperatures, yielding carbonic acid and water. Heated to 100° for about 10 hours in sealed tubes with water and *peroxide of lead*, it yields carbonate and formiate of lead. In the preparation of this compound by the process above given, part of it appears to be oxidised by oxygen derived from the oxalate of silver: for the volume of carbonic acid evolved is greater than that of the carbonic oxide (they should be equal according to the above equation); and towards the end of the operation oxalic acid sublimes in crystals:  $C^4H^4O^4 + 6O = C^4H^2O^3 + 2HO$ . — 2. With red *iodide of phosphorus*, it yields iodide of methylene and is at the same time partially carbonized. — 3. When *ammonia-gas* is passed over pulverized oxide of methylene, heat is evolved, a watery liquid is separated, and a volatile crystalline substance is formed possessing basic properties.

**Combinations.** Bioxymethylene does not dissolve in *water*, *alcohol* or *ether*, when merely boiled with it for a short time; but when heated with water to 100° in a sealed tube for several hours, it dissolves completely, forming a solution, which, when evaporated in *vacuo*, leaves a residue consisting chiefly of unaltered bioxymethylene.

### Iodide of Methylene. $C^2H^2I^2$ .

BUTLEROW. *Ann. Pharm.* 107, 110; 111, 242.

Produced by the action of iodoform on ethylate of sodium; [possibly thus:



The best result is obtained when 9 at. ethylate of sodium (in not too concentrated solution and not turned brown by exposure to the air) are gradually added to 4 at. pulverized iodoform. On adding water to the product, iodide of methylene separates as an oily liquid which must be washed with water and rectified over chloride of calcium.

Yellowish, strongly refracting liquid of sp. gr. 3.342 at + 5°; at + 2° it solidifies to a mass of broad, shining, crystalline laminæ.

						Butlerow.	
2 C .....	12	...	4.47	.....	4.88	...	4.56
2 H .....	2	...	0.75	.....	0.82	...	0.85
2 I .....	254	...	94.78	.....	95.30	...	95.68
<hr/>							
$C^2H^2I^2$ .....	268	...	100.00	.....	101.00	...	101.09

Butlerow regards it as probable that the substance which Serullas obtained (*Ann. Chim. Phys.* 25, 311), by the action of pentachloride of phosphorus on iodoform, was iodide of methylene; also the compound which Brüning produced (*Ann. Pharm.* 104, 187), by treating iodoform with alcoholic potash. This last substance gave by analysis

4.39 to 4.59 p. c. C, and 93.55 to 92.84 I, numbers which do not agree very well with the composition of iodide of methylene. Brünig assigns to this compound the formula  $C^2H^2O$ , which requires 4.36 C, and 92.35 I. Its sp. gr. in the liquid state is 3.345. It solidifies in the crystalline form at  $6^\circ$ ; and boils between  $181^\circ$  and  $182^\circ$ . Vapour-density 9.55 at  $208^\circ$ , and also at  $250^\circ$ ; by calculation from the formula  $C^2H^2O$ , for a condensation to 2 volumes, it is 9.50.

Iodide of methylene is not decomposed by *potassium* at ordinary temperatures, but on applying heat, an evolution of gas immediately takes place, ending with a violent explosion. *Sodium* acts in a similar manner, but the explosion is less violent. When *sodium-amalgum* containing  $\frac{1}{2}$  of sodium is rubbed to powder and heated with iodide of methylene, a combustible gas is evolved, and iodide of sodium is formed, together with a blackish carbonaceous substance which glimmers away when set on fire. The gas is chiefly hydrogen, but appears to contain a small quantity of methylene; for when it is passed into bromine, after having been freed from vapours of iodide of methylene and of alcohol by passing first through alcohol and then through water, and the bromine is afterwards treated with potash, a small quantity of oil is left undissolved having an odour like that of Dutch liquid. — Iodide of methylene treated with *acetate of silver* is converted into acetate of methylene.

*Chloride of Methylene*,  $C^2H^2Cl^2$ , is produced by the action of chlorine on iodide of methylene. When chlorine gas is passed into iodide of methylene contained in a retort under water, and the retort is gently heated, a very volatile liquid passes over into the receiver, and iodine separates in the crystalline form. The oily liquid, which is chloride of methylene, is purified by heating it with chlorine and a few drops of potash-ley, drying over chloride of calcium, and rectifying.

It is a colourless liquid, heavier than water, but lighter than the iodide: for fused chloride of calcium sinks to the bottom of it. It has a penetrating odour very much like that of chloroform. Does not solidify in a mixture of snow and salt. Boils at about  $40^\circ$ .

Butlerow.

2 C .....	12	....	14.12	
2 H .....	2	....	2.35	
2 Cl .....	71	....	83.53	..... 82.21

---

$C^2H^2Cl^2$  ..... 85 .... 100.00

According to the known boiling points of the chlorides of butylene, propylene, and ethylene, that of chloride of methylene should be  $65^\circ$  instead of  $40^\circ$ . Now according to Wurtz, the difference of boiling point between chloride of ethylene and the isomeric body chloride of ethylidene is  $25^\circ$ . (See *additions to vol. viii*, p. 376. If then this same difference between the boiling points of chloride of methylene, and chloride of methylidene, is also  $25^\circ$ , the latter should boil at  $40^\circ$ , as the compound now under consideration actually does. Hence Butlerow thinks it not improbable that this compound is really *chloride of methylidene*, and consequently that the iodide of methylene above described, is also really an iodide of methylidene; but till this point is satisfactorily ascertained, it is best to designate these bodies as methylene-compounds.

*Bromide of Methylene*  $C^2H^2Br^2$ . — Produced by the action of bromine on iodide of methylene. (Butlerow.)

## Acetate of Methylene.



BUTLEROW. *loc. cit.*

*Biacetate of methyl-glycol, Zweifach-essigsäures Methyl-glycol.*

*Formation.* By the action of iodide of methylene on acetate of silver ;

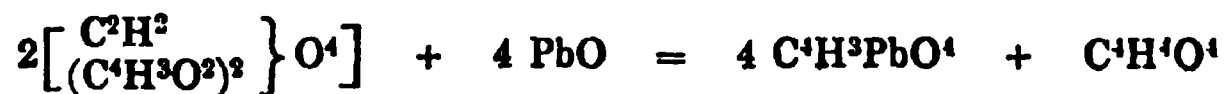


*Preparation.* An intimate mixture of the two substances in equivalent quantities, with the addition of crystallisable acetic acid, is heated to 100° for some hours ; the resulting mass is distilled in an oil-bath ; the distillate is rectified, the portion which distils above 150° being collected apart ; this portion is saturated with lime ; and the acetate of lime is dissolved out by water. Acetate of methylene then separates as an oil, which is dried by chloride of calcium, and freed from the last traces of iodide of methylene and acetic acid by distillation over dry acetate of silver and a small quantity of quick lime.

*Properties.* Oily liquid, heavier than water, and having an aromatic taste with pungent after-taste.

Butlerow.							
10 C	.....	60	...	45.45	.....	45.04	... 44.83
8 H	.....	8	...	6.06	.....	6.13	... 6.14
8 O	.....	64	...	48.49	.....	48.83	... 49.03
<hr/>							
C <sup>10</sup> H <sup>8</sup> O <sup>8</sup>	.....	132	...	100.00	.....	100.00	... 100.00

Acetate of methylene dissolves in water to a certain extent without decomposition ; but when enclosed in a sealed tube with a quantity of water not sufficient to dissolve it at ordinary temperatures, and heated to 100° for twenty hours, it is dissolved and completely decomposed, yielding acetic acid and a solid volatile substance which dissolves readily in water and remains as a white residue when the solution is evaporated in vacuo. — Acetate of methylene boiled with aqueous alkalis (potash or baryta-water) or heated with them in sealed tubes, is decomposed, yielding an acetate of the alkali, and perhaps also a small quantity of formiate. Neither in this decomposition nor in that by water, is any hydrate of methylene (methyl-glycol) formed. — When acetate of methylene is heated with water and oxide of lead in a sealed glass tube, acetate of lead is formed, together with *bioxymethylene* (p. 389).



It is also decomposed by ammonia, but neither in this case is any methyl-glycol formed. — These facts seem to show that methyl-glycol has no existence. (Butlerow.)

Page 287.

**Chloride of Methyl**  $C^2H^3Cl$ . — This compound was first obtained by Dumas and Peligot, who prepared it by the action of a mixture of sulphuric acid and chloride of sodium on wood-spirit. Bunsen obtained a gas having the same composition and physical properties by the action of heat on basic perchloride of cacodyl (ix, 347); and Kolbe & Warrentrapp (*Ann. Pharm.* 76, 37) also obtained a gas of the same composition by leaving a mixture of equal volumes of marsh-gas and chlorine exposed to diffused daylight. Gerhardt (*Traité de Chim. org.* i, 566) regarded the first only of these products as  $C^2H^3Cl$ ; the two latter as  $C^2H^2Cl.H$ .

Baeyer (*Ann. Pharm.* 103, 181) has endeavoured to decide upon the identity or non-identity of the gases obtained by the above three methods by examining their absorbability in water. — 1. For the gas obtained by the decomposition of basic perchloride of cacodyl, he found the co-efficient of absorption\* in water to be at  $7^\circ = 5.304$ ; at  $14^\circ = 4.172$ ; at  $20^\circ = 3.462$ ; at  $25^\circ = 3.034$ . This gas also forms with water below  $6^\circ$  a solid colourless hydrate which separates in amorphous films when the gas is passed into cold water, but may be obtained by slow cooling in large crystals, apparently rhombic prisms. — 2. The gas produced by the action of sulphuric acid and chloride of sodium on wood-spirit likewise forms this hydrate, and the pure gaseous chloride of methyl thus obtained exhibited the same degree of absorbability in water. — 3. The substitution-product obtained by the action of chlorine on marsh-gas did not form any hydrate with water, and exhibited a much lower degree of absorbability (0.08 at  $14^\circ$ ). Hence Baeyer concludes that the gas produced by the decomposition of basic perchloride of cacodyl is identical with chloride of methyl, but that the substitution-product of the action of chlorine on marsh-gas is merely isomeric with it.

According to Berthelot, on the other hand, the last-mentioned gas is really chloride of methyl, and may be converted into methylic alcohol by the action of potash, &c. (see xii, 478.)

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Page 319.

**Bimethylamine.**  $(C^2H^3)^2.H.N$ . Gössman, by decomposing sulphite of aldehyde-ammonia with lime, obtained an organic base, having the composition  $C^4H^7N$ , which he supposed to be ethylamine (*vid* ix, 26; also *Ann. Pharm.* 91, 122). It has however been shown by Petersen (*Ann. Pharm.* 102, 317) that the base thus obtained is not ethylamine, but the metameric substance bimethylamine. — This was proved by subjecting the base to the action of iodide of ethyl, whereby the iodide of *bimethyl-biethylium*  $(C^2H^3)^2(C^2H^5)^2N$  was produced (see next page).

Bimethylamine may also be obtained from sulphite of aldehyde-ammonia, without the action of lime, viz. 1. By heating the compound to  $140^\circ$  or  $150^\circ$  in a sealed tube, and boiling the resulting brown mass

\* The coefficient of absorption of a gas in a liquid, is the volume of gas, reduced to  $6^\circ C$  and 0.760 met. pressure, which is absorbed by a unit of volume of the liquid under the same pressure.

with hydrochloric acid. Sulphur then separates; the aldehyde is partly given off, partly converted into acetic acid; a small quantity of sulphuric acid is also formed; and on distilling the liquid with potash, dimethylamine is given off, while acetate and sulphate of potash remain behind. — 2. By heating an aqueous solution of sulphite of aldehyde-ammonia for some time, and afterwards distilling it. An ammoniacal liquid then passes over at first; afterwards sulphur separates; and between 125° and 150°, there pass over — together with sulphide of ammonium and sulphite and acetate of ammonia — oily drops of liquid having the odour of garlic, and consisting of *bisulphide of ethyl*  $C^4H^6S^2$ , the quantity of which increases when the dried contents of the retort are heated with water somewhat more strongly than before. The liquid gave by analysis 51.8 p. c. sulphur, the formula  $C^4H^6S^2$  requiring 52.46 p. c. — After the sulphide of ethyl has passed over, dimethylamine is evolved together with carbonic acid, and in the retort there remains sulphate of dimethylamine, together with ammoniacal salts. (Petersen.)

Dimethylamine is volatile, with a strong ammoniacal odour: gaseous at ordinary temperatures. Its boiling point appears to lie between 10° and 15°.

*Hydrochlorate of Dimethylamine*  $C^4H^9N.HCl$ , formerly mistaken for hydrochlorate of ethylamine, forms lamino-crystalline masses, which are very hygroscopic and easily fusible. It dissolves readily in water, with nearly equal facility in alcohol, much less in ether. Gössman's analysis (*Ann. Pharm.* 91, 122) gave 43.0 p. c. chlorine, the formula requiring 43.55.

*Platinum-salt*  $C^4H^9N.HCl.PtCl^3$ . — Yellow precipitate rather sparingly soluble in water, less in alcohol and ether.

Analysis gave 39.3 to 39.6 p. c. platinum, the formula requiring 39.31.

**Dimethyl-diethylammonium.**  $(C^2H^5)^2(C^4H^9)^2N$ . — The iodide of this radical is obtained by passing gaseous dimethylamine (evolved from the hydrochlorate by distillation with potash) into iodide of ethyl, by which it is readily absorbed, and heating the resulting liquid to 100° in a sealed tube which then becomes filled with white tabular crystals of the iodide, easily soluble in water and alcohol.

The *Chloroplatinate*  $(C^2H^5)^2(C^4H^9)^2NCl.PtCl^3$  was prepared by decomposing the iodide with oxide of silver, saturating the alkaline filtrate with hydrochloric acid, and adding bichloride of platinum. The solution concentrated by evaporation deposited the platinum-salt in yellowish prisms or tabular crystals moderately soluble in water, sparingly in alcohol and ether.

					Petersen.
12 C	72.0	...	23.43	.....	23.43
16 H	16.0	...	5.22	.....	52.31
N	14.0	...	4.55		
3 Cl	106.5	...	34.67		
Pt	98.7	...	32.13	.....	32.28
<hr/>					
$C^{12}H^{16}NCl.PtCl^3$	307.2	...	100.00		

Page 320.

*Trimethylamine* ( $\text{C}^3\text{H}^3$ ) $^3\text{N}$ . — This base has been found, by Dessaignes, in human urine. — On distilling a considerable quantity of the urine, a liquid was obtained which smelt strongly of ammonia and also like sea-fish, and turned reddish when saturated with hydrochloric acid. This solution, when concentrated, deposited a large quantity of chloride of ammonium; and on evaporating the mother-liquor to dryness, digesting the residue with alcohol, mixing the alcoholic solution with bichloride of platinum and recrystallising several times, the platinum-salt of trimethylamine was obtained in fine crystals.

					Dessaignes.
6 C .....	36.0	....	13.58	.....	13.85
10 H .....	10.0	....	3.77	.....	3.94
N .....	14.0	....	5.26	.....	5.32
3 Cl .....	106.5	....	40.22	.....	40.23
Pt .....	98.7	....	37.17	.....	37.02
<hr/>					
$\text{C}^6\text{H}^9\text{NCl.PtCl}^2$ .....	165.2	....	100.00	.....	100.36

65 litres of liquid obtained by the distillation of previously concentrated urine yielded 2,200 grms. of chloride of ammonium and only 17 grms. of the platinum-salt of trimethylamine, corresponding to 3.7 grms. of the base (*Ann. Pharm.* 100, 218; *Compt. rend.* 43, 670).

Dessaignes has also found trimethylamine in small quantity in the blood of the calf, 12 hours after it had been taken from the animal, the blood when shaken up with milk of lime emitting the characteristic crab-like odour of trimethylamine, and yielding, when distilled with lime, an alkaline distillate from which a small quantity of chloroplatinate of trimethylamine was obtained in the manner above described. The blood, immediately after being taken from the vessels, gave no evidence of the presence of trimethylamine. Hence Dessaignes concludes that blood, as well as urine, contains a small quantity of some easily decomposable compound which yields trimethylamine as one of its products of decomposition. (*J. Pharm.* 32, 43.)

According to Wittstein (*Vierteljahrsschrift, pr. Pharm.* 8, 33), trimethylamine [or, perhaps, propylamine] exists in *Chenopodium vulvaria* and in fresh-water crabs.

[For the description of the organic bases produced by the action of bromide of ethylene on trimethylamine, and of numerous other organic bases recently discovered by Dr. Hofmann, see the next volume of this work.]

Page 320.

## Mercury-compounds of Tetramethylium.

H. RISSE. *Ann. Pharm.* 107, 223.

$\alpha$ . ( $\text{C}^3\text{H}^3$ ) $^4\text{NI}$  + 2HgI. — Produced: 1. By the action of metallic mercury on an alcoholic solution of teriodide of tetramethylium (xii, 321)

$(C^2H^3)^4I^3 + 2Hg = (C^2H^3)^4I \cdot 2HgI$ . — Separates on cooling in small light yellow prisms, moderately soluble in cold alcohol. — 2. By adding iodide of mercury to an excess of iodide of tetramethylum in hot alcoholic solution. The excess of the latter salt then crystallises out first, and on cooling the light yellow salt separates. — 3. By treating the following salt *b* for some time with metallic mercury, mercurous iodide being formed at the same time.

Risse.					
8 C .....	48	...	7.33		
12 H .....	12	...	1.83		
N .....	14	...	2.14		
2 Hg .....	200	...	30.53	.....	30.04 to 30.27
3 I .....	381	...	58.17	.....	58.54 ,, 58.18
<hr/>					
$(C^2H^3)^4I \cdot 2HgI$ ....	655	...	100.00		

*b.*  $(C^2H^3)^4NI \cdot 3HgI$ . Produced: 1. By the action of metallic mercury on penta-iodide of tetramethylamium. The reaction is not so simple as that by which the salt *a* is produced, mercurous iodide being found at the same time. The supernatant wine-yellow solution deposits the salt *b* on cooling, in fine lemon-yellow waxy scales, generally mixed with the slender light yellow crystals of the salt *a* produced by the decomposition of *b*; their formation may be prevented by stopping the process as soon as the alcoholic solution becomes decolorised. — 2. When a hot alcoholic solution of iodide of tetramethylum is mixed with excess of iodide of mercury, the salt *b* crystallises out on cooling, and the mother-liquor yields crystals of iodide of mercury.

Risse.							
				(1.)                      (2.)			
8 C .....	48	...	5.44				
12 H .....	12	...	1.36				
N .....	14	...	1.59				
3 Hg .....	300	...	34.01	... ..	34.55	35.04	... 35.11
4 I .....	508	...	57.60	.....	57.30	57.22	... 57.33
<hr/>							
$(C^2H^3)^4NI \cdot 3HgI$ .....	882	...	100.00				

(For the *Arsenides of Methyl*, see additions to vol. ix.)

*Zinc-methyl.* — (Frankland. *Ann. Pharm.* 111, 62.) — The action of zinc upon iodide of methyl is different according as the materials are heated in a copper digester or in a sealed glass tube. In the latter case zinc-methyl is easily produced; in the former, decomposition likewise takes place, between the temperatures 120° and 200°; but at the lower temperatures between these limits, it is imperfect, and near the higher limit, the product consists, not of zinc-methyl, but of permanent gases. The cause of this difference appears to be that in the glass tube only half immersed in an oil-bath, a continual distillation takes place, the vapour formed in the lower part of the tube condensing in the



upper and running down again upon the zinc: whereas the copper-digester being made of a good conducting material, all its parts are nearly at the same temperature and no such distillation can take place.

To enable the formation of zinc-methyl to go on with facility in the copper-digester, it is necessary to mix the iodide of methyl either with common ether or with methylic ether. The decomposition then takes place more easily than that of iodide of ethyl by zinc, but the product obtained is not pure zinc-methyl, but contains in addition oxide of ethyl and oxide of methyl.

*Zinc-methyl with Oxide of Ethyl*  $2\text{C}^4\text{H}^6\text{Zn}^2 + \text{C}^8\text{H}^{10}\text{O}^2$ . — Three fluid ounces of zinc-methyl mixed with an equal volume of anhydrous ether and heated with zinc to  $100^\circ$  in a copper-digester for 6 hours, were completely decomposed; and on opening the digester, very little gas escaped, the whole of the iodide of methyl having been converted into zinc-methyl. The product heated in an oil-bath began to distil at  $90^\circ$ , and the distillation was complete before the thermometer had risen to  $140^\circ$ . On rectifying the distillate, it began to boil at  $35^\circ$ ; and the thermometer then rose quickly to  $48^\circ$ , between which temperature and  $51^\circ$ , nearly the whole of the remaining portion, constituting the greater part of the product, passed over. This liquid which distilled over between these two last-mentioned temperatures, possessed the intolerable odour of zinc-methyl, was extremely inflammable, and exhibited generally the properties of zinc-methyl. By analysis, however, it gave considerably too much carbon and hydrogen; and the last portion of the distillate, which came over between  $51^\circ$  and  $57^\circ$ , exhibited the composition of a mixture of 2 at. zinc-methyl ( $\text{C}^4\text{H}^6\text{Zn}^2$ ) with 1 at. ether ( $\text{C}^8\text{H}^{10}\text{O}^2$ ), with which also the observed vapour density, 3.1215, agrees very nearly.

					Frankland.
16 C .....	96.0	....	36.85	.....	36.37
22 H .....	22.0	....	8.33	.....	7.99
4 Zn .....	130.1	....	49.26		
2 O .....	16.0	....	6.06		
<hr/>					
$2\text{C}^4\text{H}^6\text{Zn}^2 + \text{C}^8\text{H}^{10}\text{O}^2$ .....	264.1	....	100.00		

	Vol.	Density.
Zinc-methyl vapour .....	4	6.5672
Ether-vapour .....	2	2.5567
<hr/>		
Vapour of mixture .....	6	9.1239
	2	3.0413

It does not appear possible to obtain pure zinc-methyl by the action of zinc on iodide of methyl mixed with ether, although a similar process succeeds so well in the preparation of zinc-ethyl (x, 730). Pure iodide of methyl is not decomposed by zinc at  $100^\circ$ , in the copper digester; an addition of 3 or 4 per cent. of ether is sufficient to cause the decomposition to take place though not completely; and it is not possible to separate the zinc-methyl from the residual iodide of methyl, or from the ether. (Frankland.)

*Zinc-methyl with Oxide of Methyl*  $2\text{C}^4\text{H}^6\text{Zn}^2 + \text{C}^4\text{H}^6\text{O}^2$ . — Three fluid ounces of iodide of methyl were introduced, together with the proper quantity of zinc, into the copper-digester; gaseous oxide of methyl previously dried by chloride of calcium was forced by a condensing syringe



into the digester till a volume of liquid methylic ether was condensed, about equal to that of the zinc-methyl, and the digester was then heated for three days in the water-bath. The product obtained by subsequent distillation of the mass was very rich in zinc-methyl, and was easily freed from a little undecomposed iodide of methyl by means of sodium. On rectifying the liquid thus obtained, the greater part distilled over at  $43^{\circ}$ , the remainder between  $43^{\circ}$  and  $48^{\circ}$ . The two portions gave by analysis 29.54 and 29.59 p. c. carbon and 7.11 and 7.20 hydrogen, numbers nearly agreeing with the formula  $2C^4H^6Zn^2 + C^4H^6O^2$  which requires 30.49 C and 7.62 H. (Frankland.)

### Mercuric Methyl. $C^2H^3Hg$ .

G. B. BUCKTON. *Proc. Roy. Soc.* 9, 91; *Chem. Gaz.* 1858, 117; *Ann. Pharm.* 108, 103.

Compounds of mercurous methyl  $C^2H^3Hg^2$ , were prepared by Frankland in 1853 (*Ann. Pharm.* 85, 381), and by Strecker in 1854 (*Compt. rend.* 39, 57).

*Preparation.* 1. By the action of cyanide of potassium on iodide of mercurous methyl. The latter compound, prepared as described at page 110, vol. ix, and free from every trace of iodide of methyl, is triturated in a mortar with finely pulverised cyanide of potassium, and the mixture is distilled by small portions over a gas-lamp. Gaseous products are then evolved; iodide of potassium is formed; cyanogen is set free, and remains in the form of paracyanogen; and mercuric methyl passes over in the form of a heavy liquid which may be purified by washing with water and rectifying over chloride of calcium. The essential part of the decomposition is represented by the equation :



2. By distilling iodide of mercurous methyl with hydrate of potash or lime :



This mode of preparation is not so easy as the former.

*Properties.* Colourless, strongly refracting liquid, having a faint and somewhat sweetish taste. Sp. gr. 3.069. Boiling point between  $93^{\circ}$  and  $96^{\circ}$ . Vapour density 8.29.

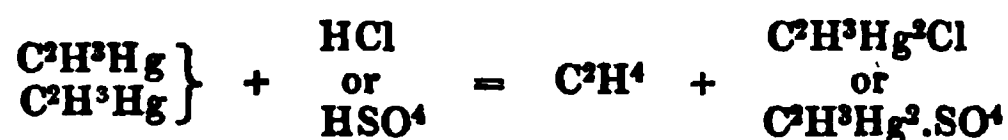
					Vol.		Density.
2 C .....	12	...	10.43	.....	C-vapour .....	2	..... 0.8320
3 H .....	3	...	2.61	.....	H-gas .....	3	..... 0.2079
Hg .....	100	...	86.96	.....	Hg-vapour .....	1	..... 6.9300
<hr/>							
$C^2H^3Hg$ .....	115	...	100.00	.....	Vap. of $C^2H^3Hg$	1	..... 7.9699

*Decompositions.* 1. Mercuric methyl is incapable of uniting as a whole with *oxygen*, *chlorine*, or other electro-negative elements, being completely decomposed by them. It is very inflammable and burns with

a bright flame, giving off vapours of mercury. — 2. *Iodine* and *bromine* act upon it with violence and a hissing noise, eliminating methyl-gas and forming iodide or bromide of mercurous methyl :



3. With strong *sulphuric* or *hydrochloric acid*, it gives off marsh-gas and forms crystals of sulphate or chloride of mercurous methyl.



4. With dilute acids and metallic *zinc* it yields metallic mercury and gaseous products. The salts of mercurous methyl are decomposed in like manner.

*Combinations.* Mercuric methyl is nearly insoluble in *water*. It dissolves *phosphorus* readily and *sulphur* in small quantity.

With *bichloride of tin*, it forms a crystalline compound, which is decomposed by water, with formation of  $\text{C}^2\text{H}^3\text{Hg}^2\text{Cl}$  and a soluble tin-salt. — The chloride  $\text{C}^2\text{H}^3\text{Hg}^2\text{Cl}$  is also formed by the action of terchloride of phosphorus.

Heated with *mercuric iodide*,  $\text{HgI}_2$ , it forms iodide of mercurous methyl  $\text{C}^2\text{H}^3\text{Hg}^2\text{I}$ .

It is very soluble in *alcohol* and in *ether*, and readily dissolves *caoutchouc* and *resins*.

*Nitrate of Mercurous Methyl.*  $\text{C}^2\text{H}^3\text{Hg}^2.\text{NO}^3$ . — Obtained by treating an alcoholic solution of iodide of mercurous methyl (iodide of hydrargomethyl, ix, 110) with nitrate of silver, and evaporating the filtrate in vacuo. Crystallizes in nacreous laminæ, very soluble in water sparingly in alcohol. At  $100^\circ$ , it melts to a colourless liquid which solidifies in a crystalline mass on cooling. Its solution is not precipitated by potash or baryta-water. Hydrochloric acid and soluble chlorides precipitate chloride of *mercurous methyl* in nacreous laminæ. The crystallised nitrate gave by analysis 18.9 p. c. anhydrous nitric acid ( $\text{NO}^3$ ) agreeing with the formula  $\text{C}^2\text{H}^3\text{Hg}^2.\text{NO}^3 + \text{Aq.}$  (Strecker, *Ann. Pharm.* 92, 79.)

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Page 330.

*Iodoform.*  $\text{C}^2\text{HI}^3$ . — The crystals of this compound are hexagonal combinations,  $oP \cdot P$ ;—for  $P$ , the ratio of the secondary axes to the principal axis is  $0.9025:1$ ;— $P:P$  in the terminal edges =  $133^\circ 36'$ ; in the lateral edges =  $104^\circ 0'$ . (Rammelsberg, *Jahresber.* 1857, p. 431. Kokscharow, *Chem. Centr.* 1857, 524.)

For the decomposition of iodoform by ethylate of sodium and by alcoholic potash, see page 390 of this volume. For the action of light on its solution in bisulphide of carbon, see Humbert, *N. J. Pharm.* 29, 352.

*Sulphoform.*  $\text{C}^2\text{HS}^3$ ? By heating a mixture of 1 pt. iodoform and 3 pts. of cinnabar, Bouchardat obtained a small quantity of yellow oil, which he supposed to be sulphoform. According to Eggert, however (*Chem. Centr.* 1857, 513), the only liquid thus obtained (amounting to  $4-5\frac{1}{2}$  per cent. of the iodoform), is bisulphide of carbon.

Page 342.

*Chloroform.* — This body is produced, together with hydrochloric acid, by the action of nascent *hydrogen* (evolved from hydrochloric or dilute sulphuric acid by the action of zinc) on bichloride of carbon  $C^2Cl^4$  :



Chloroform itself is reduced by nascent hydrogen to the compound  $C^2H^2Cl^3$  which boils at a lower temperature. (Geuther, *Ann. Pharm.* 107, 212.)

A mixture of chloroform vapour and *ammonia-gas* is decomposed at a heat approaching to dull redness, yielding chloride and cyanide of ammonium:



If the temperature is raised too high, a brown substance is deposited, probably paracyanogen produced from the cyanide of ammonium. When a solution of ammonia in absolute alcohol is heated with chloroform to between  $180^\circ$  and  $190^\circ$ , formiate of ammonia may be produced as well as cyanide; in many instances also, neither of these salts is formed, but a considerable quantity of a brown mass probably consisting for the most part of paracyanogen. (Ethylamine may also be formed; but its production is independent of the chloroform, and results merely from the mutual action of the ammonia and the alcohol.) (Heintz, *Pogg.* 98, 263; *Ann. Pharm.* 100, 369.)

A mixture of chloroform and *aniline* in equal volumes heated in a sealed tube to  $180^\circ$  —  $190^\circ$ , yields hydrochlorate of aniline and hydrochlorate of *formyl-biphenylbiamine* a base formed by the replacement of 3 at. hydrogen in 2 at. aniline by the triatomic radical  $C^2H$ , giving the formula,  $C^{24}H^{11}(C^2H)^{11}N^2 = C^{26}H^{12}N^2$  :



Chloroform does not act on aniline at ordinary temperatures. (Hofmann, *Chem. Gaz.* 1858, 259.)

A mixture of potash, alcohol, and chloroform (or bichloride of carbon) heated in sealed tubes to  $100^\circ$  for a week, yields olefiant gas together with formic acid (Berthelot, *N. Ann. Chim. Phys.* 54, 87).

Chloroform is not decomposed by *sodium*, even when heated with it to  $200^\circ$  in a sealed tube (Heintz).

For testing the purity of chloroform, Roussin (*N. J. Pharm.* 34, 206) recommends the use of *binitrosulphide of iron*  $Fe^3S^5HN^2O^4$  (a salt obtained by the action of ferric chloride or sulphate on a mixture of sulphide of ammonium and nitrite of potash, *N. Ann. Chim. Phys.* 52, 285). Pure chloroform shaken up with this salt remains colourless; but if it contains alcohol, ether, or wood-spirit, it acquires a dark colour.

Urea.

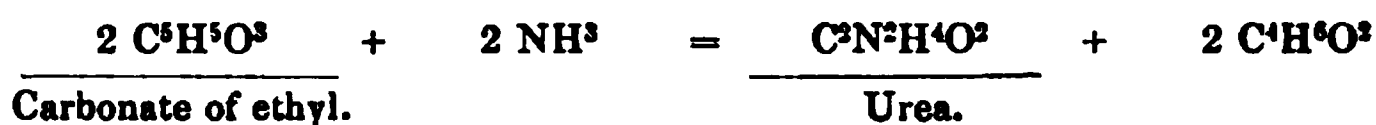
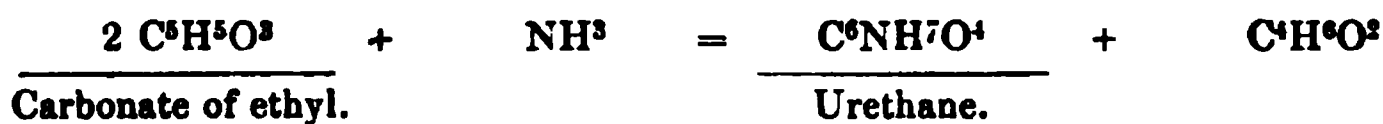
*Occurrence in the Animal Body.* — Wurtz has shown (*Compt. rend.* 49, 53,) that urea exists in chyle and lymph. The following table gives the quantities of urea found in the blood, chyle and lymph of several animals :

Name of animal.	Diet.					Quan. of urea in 1000 grams.		
						Blood.	Chyle.	Lymph.
Dog    ....	Meat        ....					0·089	....	0·158
”       ....	”           ....					”	0·183	
Cow     ....	Dry lucern   ....					0·192	0·192	0·193
Bull    ....	Lucern and oil-cake   ....					....	0·189	
Another bull    ....	Oil-cake (before rumination)   ....					....		
						arterial		
Ram     ....	Ordinary diet (rumination sus- pended)					0·248	0·230	
Sheep   ....	”                ”					....	0·071	
Horse   ....	”                ”					....	....	{ 0·126 0·112

Poisseuille & Gobley (*Compt. rend.* 49, 164) have found that the quantity of urea in the arterial blood of various animals, both herbivorous and carnivorous, viz. the bull, cow, horse, and dog is, on the average, 0·220 grm. per kilogramme, the limits being 0·185 and 0·241. They find also, by comparing the quantity of urea conveyed to the kidneys in 24 hours with the quantity excreted in the same time in the urine, that the greater part of the urea conveyed to the kidneys by the blood is not eliminated by these organs. A man through whose kidneys there passed 1000 kilogrammes of blood per day, containing  $1000 \times 0\cdot220 = 220$  grms. of urea, discharged in the same time only 20 grms. in the urine, hence 200 grms. must have returned into the circulation. A dog through whose kidneys there passed in 24 hours 332 kilogrammes of blood, containing  $332 \times 0\cdot220 = 73$  grammes of urea, voided in the urine only a few grammes; hence from 60 to 65 grms. of urea per day must have entered into the circulation. — From these facts the authors infer that urea is not essentially an excrementitious substance, but contributes in some way to the metamorphosis of the tissues. In accordance with this view they find that in many instances the blood which issues from an organ contains *less* urea than the blood which enters the same organ : thus the blood of the right cavities of the heart of a horse was found to contain 0·225 grm. urea per kilogramme; that of the left cavities only 0·174 grm. The blood of the carotid artery of a bull contained 0·289 grm. urea per kilo-

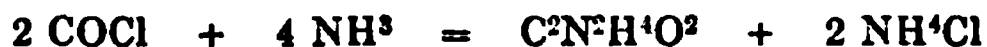
gramme, that of the jugular vein only 0.209. — In other cases, on the contrary, the blood after leaving an organ was found to be richer in urea than on entering it,—the difference appearing to depend upon the physiological condition of the animal.

*Formation.* 1. *By the action of Ammonia on Carbonate of Ethyl.* When carbonate of ethyl is heated with ammonia to 100° in a sealed tube, nothing but urethane (carbonate of ethyl, ix, 274) is produced; but on heating the mixture to 180°, the urethane is converted by the excess of ammonia into carbamide or urea:



Urethane sublimes in the empty part of the tube; and if the watery liquid be evaporated to dryness, and the residue heated for some time to 100°, more urethane volatilises, and urea remains behind, still however mixed with a little urethane, from which it may be freed by washing with ether. It then exhibits the physical characters of urea and forms the characteristic crystalline salts with nitric and oxalic acids. — This mode of formation shows that urea is identical with carbamide (Natanson, *Ann. Pharm.* 98, 287).

2. *By the Action of Ammonia on Phosgene.* — The product of this action is a white saline mass, consisting of chloride of ammonium mixed with carbamide, which Regnault, who first obtained it (*Ann. Chim. Phys.* 69, 180), regarded as isomeric, but not identical with urea:



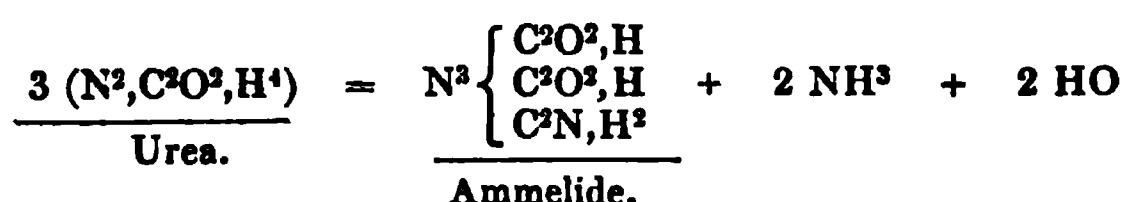
Natanson has, however, shown that the compound thus formed is really urea. The quantity of it produced is small in comparison with that of the sal-ammoniac, unless the two gases have been carefully freed from moisture. To isolate the urea, the chloride of ammonium is decomposed by excess of baryta-water; the liquid is evaporated to dryness in vacuo over sulphuric acid; the urea is dissolved out from the residue by absolute alcohol; the alcoholic solution is evaporated; the residue dissolved in water, and the solution treated with carbonate of ammonia to remove any baryta that may still be present; and the concentrated liquid is treated with nitric acid, which precipitates nitrate of urea.

According to Béchamp (*N. Ann. Chim. Phys.*), urea is produced by the oxidation of albumen (white of egg), blood-fibrin, muscular fibrin, and gluten, with permanganate of potash. According to Städeler, on the contrary, the oxidation of albuminous substances by permanganate of potash produces not a trace of urea, but a somewhat considerable quantity of benzoic acid (*J. pr. Chem.* 72, 251).

On the constitution of urea, see Weltzien, *Ann. Pharm.* 100, 190; Heintz, *J. pr. Chem.* 72, 129.

*Decompositions.* 1. When 1 at. urea is heated with 1 at. *anhydrous phosphoric acid* to about 40° in a flask connected with several cooled

U-tubes, the temperature quickly rises to  $130^{\circ}$  —  $140^{\circ}$ , and a large quantity of cyanic acid condenses in the first tube, while the substance condensed in the second consists chiefly of cyamelide (insoluble cyanuric acid, ix, 462). — There is also formed a small quantity of another body closely related to cyanuric acid, but more soluble in water, containing no water of crystallisation, and crystallising in transparent silvery prisms or groups of needles. — Another part of the urea splits up into water and bodies belonging to the group of cyanamines, among which ammelide is found:



(Weltzien, *Ann. Pharm.* 107, 219.)

2. With *hypochlorite of soda*, urea yields chloride of sodium, carbonic acid, water and nitrogen :



The measurement of the volume of nitrogen remaining after the absorption of the carbonic acid by potash, serves as a measure of the quantity of urea decomposed. This method is proposed by Leconte (*Compt. rend.* 47, 237) for the estimation of urea in urine. By decomposing 0.100 grm. urea with hypochlorite of soda, Leconte obtained only 34 cc. nitrogen, instead of the calculated quantity, 37 cc., whence he adopts the former number as the basis of this calculation.

*Combinations.* *a. Basic Hydrochlorate of Urea*,  $2\text{C}^2\text{N}^2\text{H}^4, \text{HCl}$ . — Obtained by adding 1 at. hydrochloric acid to 2 at. urea, and leaving the solution to evaporate over lime. Crystallises in long parallel accollated laminæ, slightly deliquescent. (V. Dessaignes, *N. J. Pharm.* 25, 31.)

*b. With Chloride of Ammonium.* *a.*  $\text{C}^2\text{N}^2\text{H}^4\text{O}^2, \text{NH}^4\text{Cl}$ . — A considerable quantity of urine evaporated to a syrup at the boiling heat deposits this compound in brown crystalline laminæ (mistaken for urea by Fourcroy & Vauquelin) which may be purified by draining on a funnel and recrystallisation. The compound is then obtained, sometimes in square plates half a millimetre in thickness, sometimes in long needles very much like urea itself. — From a solution of 1 at. sal-ammoniac with 1 at. urea, sal-ammoniac crystallises out first, and after its removal, the compound now under consideration is obtained. — From a solution of 2 at. urea to 1 at. sal-ammoniac, it crystallises at once. The best mode of preparing it is to evaporate urine strongly acidulated with hydrochloric acid, — It may be repeatedly crystallised in presence of an excess of urea, but it is partially decomposed by pure water. When it is heated with a quantity of water not sufficient to dissolve it completely, the liquid first deposits sal-ammoniac, and the mother-liquor then yields the original compound, which may again be decomposed by water; and the series of operations may be repeated till nothing but urea remains. — The dry compound yields cyanuric acid when heated (V. Dessaignes, *N. J. Pharm.* 32, 37).

*β.*  $2(\text{C}^2\text{N}^2\text{H}^4\text{O}^2, \text{NH}^4\text{Cl}) + \text{C}^2\text{N}^2\text{H}^4\text{O}^2, \text{HCl}$ . — Obtained by dissolving urea in aqueous hypochlorite of lime or soda, or by mixing a solution of

urea with caustic soda, and passing chlorine through the liquid as long as nitrogen continues to escape. The excess of hypochlorite is destroyed by adding a little ammonia, the liquid is evaporated to dryness, and the residue digested in a mixture of alcohol and ether. On evaporating the solution, the compound is obtained in large laminæ, which are very soluble, are decomposed by heat, precipitated by nitric acid (nitrate of urea) and give off ammonia when heated with potash (O. Beckmann, *Ann. Pharm.* 91, 367).

				Beckmann.
6 C .....	36.0	....	11.13	..... 10.46
6 N .....	84.0	....	25.97	
13 H .....	13.0	....	4.02	..... 7.18
2 NH <sup>4</sup> ....	36.0	....	11.13	..... 11.14
3 Cl .....	106.5	....	32.92	..... 32.89
6 O .....	48.0	....	14.83	
<hr/>				
323.5				.... 100.00

The deficiency of carbon and excess of hydrogen, probably arose from admixture of the salt with sal-ammoniac. In the memoir, the calculated amount of hydrogen is erroneously given as 6.49.

c. *With Chloride of Zinc*,  $C^3H^2H^4O^2, ZnCl$ . — A mixture of the alcoholic solutions of urea and chloride of zinc, evaporated over oil of vitriol, yields this compound in hard, transparent, colourless, deliquescent, crystalline geodes, which may be recrystallised from absolute alcohol (Neubauer & Kerner, *Ann. Pharm.* 101, 339).

				Neubauer & Kerner.
$C^3N^2H^4O^2$ .....	60.0	....	46.8	..... 46.7
Zn .....	32.5	....	25.5	..... 25.3
Cl .....	35.5	....	27.7	..... 27.6
<hr/>				
$C^3N^2H^4O^2, ZnCl$ .....	128.0	....	100.0	..... 99.6

d. *With Chloride of Cadmium*,  $C^3N^2H^4O^2, 2CdCl$ . — Deposited on evaporating the aqueous solutions of urea and chloride of cadmium over oil of vitriol, in large circular geodes. A mixture of the solutions of the two bodies in absolute alcohol deposits it as a white crystalline powder. It is very soluble in water.

				Neubauer & Kerner.
$C^3N^2H^4O^2$ .....	60.0	....	24.9	..... 24.4
2 Cd .....	111.5	....	46.0	..... 46.2
2 Cl .....	71.0	....	29.1	..... 29.4
<hr/>				
$C^3N^2H^4O^2, 2CdCl$ .....	242.5	....	100.0	..... 100.0

e. *With Cupric Chloride*,  $C^3N^2H^4O^2, CuCl$ . — A syrupy mixture of urea and protochloride of copper, deposits this salt after standing for some time in blue crystalline geodes which are decomposed by water.

				Neubauer & Kerner.
$C^3N^2H^4O^2$ .....	60.00	....	47.2	..... 47.2
Cu .....	31.68	....	24.9	..... 24.8
Cl .....	35.50	....	27.9	..... 27.9
<hr/>				
$C^3N^2H^4O^2, CuCl$ .....	127.18	....	100.0	..... 99.9



## Compounds of Urea with Organic Acids.

HLASIWETZ. *Wien. Akad. Ber.* 20, 207; *J. pr. Chem.* 69, 100; *Chem. Centr.* 1856, 481; *Chem. Gaz.* 1856, 221.

DESSAIGNES. *N. J. Pharm.* 32, 37.

*Succinate of Urea*,  $2\text{C}^2\text{N}^2\text{H}^4\text{O}^2, \text{C}^6\text{H}^6\text{O}^6$ . — A solution of 2 pts. urea in 1 pt. succinic acid deposits prismatic crystals with acuminate ends. They do not give off any water at  $100^\circ$ , are rather more soluble in water than oxalate of urea (ix, 171), have an acid reaction: melt at  $145^\circ$ , and decompose at a stronger heat, giving off a fibro-crystalline sublimate having the properties of succinimide. A warm solution of the crystals dissolves magnesia, oxide of zinc, and other oxides in considerable quantity and without evolution of ammonia; and at a certain degree of saturation, a basic metallic succinate separates out, while a neutral succinate remains in solution, together with pure urea. (Hlasiwetz.)

				Hlasiwetz.
12 C .....	72	...	30.25	30.55
4 N .....	56	...	23.52	23.20
14 H .....	14	...	5.88	6.26
12 O .....	96	...	40.35	39.99
<hr/>				
$2\text{C}^2\text{N}^2\text{H}^4\text{O}^2, \text{C}^6\text{H}^6\text{O}^6$ .....	238	...	100.00	100.00

*Parabanate of Urea*  $\text{C}^2\text{N}^2\text{H}^4\text{O}^2, \text{C}^6\text{NH}^2\text{O}^6$ . — A solution of 1 pt. parabanic acid and 1.5 pt. urea in boiling water deposits concentrically grouped, flat prisms, soluble in boiling alcohol, sparingly soluble in cold water. They turn reddish at  $100^\circ$  (Hlasiwetz).

				Hlasiwetz.
8 C .....	48	...	27.58	27.32
4 N .....	56	...	32.18	31.80
8 H .....	8	...	3.44	3.74
8 O .....	64	...	36.80	37.14
<hr/>				
$\text{C}^2\text{N}^2\text{H}^4\text{O}^2, \text{C}^6\text{NH}^2\text{O}^6$ .....	176	...	100.00	100.00

*Urea with Alloxantin*,  $2\text{C}^2\text{N}^2\text{H}^4\text{O}^2, \text{C}^6\text{N}^2\text{H}^5\text{O}^{10} + \text{Aq.}$  — A mixture of the solutions of 1 pt. alloxantin and 2 pts. urea in boiling water yields small, flat, drusy crystals, which when dried in vacuo give by analysis 28.96 p.c. of nitrogen, the formula requiring 29.03. They turn red at  $30^\circ$ . (Hlasiwetz.)

*Alloxan* does not appear to form a definite compound with urea.

*Tartrate of Urea*,  $\text{C}^2\text{N}^2\text{H}^4\text{O}^2, 2\text{C}^6\text{H}^4\text{O}^{10} + \text{Aq.}$  — A solution of tartaric acid and urea, the latter being rather in excess, yields after concentration to a syrup and standing for some time, prismatic crystals which have an acid reaction, and behave with metallic oxides like the succinate. Nitrogen, by analysis 8.20 per cent.; by calculation 8.40. (Hlasiwetz.)

*Tartrate of Urea and Magnesia*  $\text{C}^2\text{N}^2\text{H}^4\text{O}^2, \text{MgO}, 2\text{C}^6\text{H}^4\text{O}^{10}$ . — Obtained by dissolving magnesia in tartrate of urea. It is a granular, moderately



soluble salt, having a somewhat bitter taste. Melts very easily, giving off ammonia and leaving charcoal, which is extremely difficult to incinerate. It gave by analysis 5·83 p. c. MgO, the formula requiring 6·03 p. c. (Hlasiwetz.)

*Styphnate of Urea.* — A hot solution of 2 pts. urea and 1 pt. styphnic acid yields a salt crystallising in yellow needles or laminæ, which do not give off any water at 100°. They gave by analysis 27·07 per cent. of nitrogen, whence Hlasiwetz deduces the formula  $2C^2N^2H^4O^2, C^{12}H^2N^3O^{15}$ , requiring 27·52 per cent.

Picric acid does not appear to combine with urea.

*Citrate of Urea,*  $C^2N^2H^4O^2, 2HO, C^{12}H^5O^{11}$ . — Prepared like the tartrate, which it resembles in crystalline character.

				Hlasiwetz.
14 C .....	84	...	34·56	34·28
2 N .....	28	...	11·52	11·67
11 H .....	11	...	4·52	5·05
15 O .....	120	...	49·40	48·80
<hr/>				
$C^2N^2H^4O^2, 2HO, C^{12}H^5O^{11}$ .....	243	...	100·00	100·00

*Benzoate of Urea,*  $2C^2N^2H^4O^2, C^{14}H^6O^4$ . — Urea does not unite with benzoic acid in aqueous solution; but when urea is added by small portions to a concentrated solution of benzoic acid in absolute alcohol, the liquid being heated at each addition and then cooled, a network of crystals having the above composition is ultimately formed. The salt is decomposed by water (Dessaignes).

*Hippurate of Urea.* — Hippuric acid dissolves readily in melting urea, and the solution of the mixture in hot absolute alcohol, yields laminated crystals of a compound whose aqueous solution splits up after a while into hippuric acid, which crystallises out, and urea which remains in solution (Dessaignes).

*Meconate of Urea,*  $3C^2N^2H^4O^2, C^{14}H^4O^{14}$ . — A hot solution of 4 pts. urea and 1 pt. meconic acid deposits on cooling scaly prismatic crystals.

				Hlasiwetz.
20 C .....	120	...	31·57	31·55
6 N .....	84	...	22·10	
16 H .....	16	...	4·21	4·64
20 O .....	160	...	42·12	
<hr/>				
$3 C^2N^2H^4O^2, C^{14}H^4O^{14}$ .....	380	...	100·00	

*Gallate of Urea,*  $C^2N^2H^4O^2, C^{14}H^6O^{10}$ . — A hot solution of 2·5 to 3 pts. urea and 1 pt. gallic acids deposits on cooling, large prisms belonging to the oblique prismatic system. Their formation requires the presence of an excess of urea, and they cannot be recrystallised without adding urea to the liquid.

						Hlasiwetz.		
16 C	.....	96	...	41·74	.....	41·08	...	42·08
2 N	.....	28	...	12·17	.....	4·48	...	4·80
10 H	.....	10	...	4·34	.....	12·23	...	12·01
12 O	.....	96	...	41·75				
<hr/>								
C <sup>2</sup> N <sup>2</sup> H <sup>4</sup> O <sup>2</sup> , C <sup>14</sup> H <sup>6</sup> O <sup>10</sup>	.....	230	...	100·00				

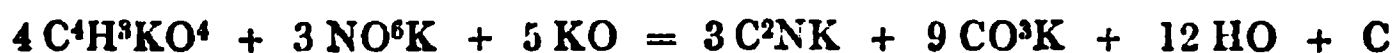
*Phloretate of Urea*,  $C^2N^2H^4O^2, 2C^{18}H^{10}O^5 + Aq.$  — See page 312 of this volume.

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Page 379.

*Formation of Cyanogen.* — According to Langlois (*N. Ann. Chim. Phys.* 52, 326), the formation of cyanogen by passing nitrogen gas over a red-hot mixture of potash and charcoal is not affected by the presence of water in the materials used. Cyanogen is produced by the passage either of moist or of perfectly dry nitrogen over a mixture of charcoal and potash, or perfectly dry charcoal and carbonate of potash strongly heated in a porcelain tube. But if instead of tubes of porcelain, tubes glazed inside with silicate of lead are used, no formation of cyanogen takes place, either with moist or with dry nitrogen; and moreover, cyanide of potassium added to the mixture of potash and charcoal disappears when heated to redness in such tubes. This effect of the glazing may account for the negative results which some chemists have obtained regarding the direct formation of cyanogen.

When a mixture of 4 pts. fused acetate of potash, 3 pts. nitre and 5 pts. caustic potash or carbonate of potash is dissolved in a small quantity of water, the solution evaporated, and the residue heated to fusion, the mass detonates at about  $250^\circ$ , and then contains a considerable quantity of cyanide of potassium:



An addition of charcoal powder to the mixture produces a slight increase in the yield of cyanogen, but by no means equal to the theoretical quantity. The largest quantity of cyanide of potassium is produced by an intimate mixture of lamp-black with acetate, nitrate, and carbonate of potash. (From 13 grms. of acetate of potash there were obtained 2.6 grms. of prussian blue.) — With starch, sawdust, soap and bitartrate of potash instead of acetate, only small quantities of cyanide of potassium were obtained.

On the preparation of *cyanide of potassium*, see Wittstein. *Vierteljahrsschr. pr. Pharm.* vii, 191; *Dingl. prol. J.*, cxlix, 157.] On the difference between the action of potash and of soda in the *formation of cyanides*, see page 385 of this volume.

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Page 430.

*Protocyanide of Iron.* — According to Fresenius (*Ann. Pharm.* 106, 210), the yellowish red flocculent precipitate produced by cyanide of potassium in ferrous salts consists essentially of ferrous cyanide  $FeCy$  containing cyanide of potassium in variable quantity (one determination gave 14.79 p.c.) The proportion of cyanide of potassium in the precipitate is

smaller, the more the iron-salt is in excess. The precipitate dissolves in cyanide of potassium, with formation of ferrocyanide of potassium; the addition of dilute potash-ley also produces the same salt, with separation of hydrated ferrous oxide. The precipitate, when exposed to the air in the moist state, takes up oxygen and turns blue.

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Page 472.

*Ferricyanide of potassium* dissolved in water is decomposed by boiling with excess of hyposulphite of soda, with separation of sulphide of iron. The slightly yellowish filtrate contains *sulphocyanide* and *ferrocyanide* of potassium, together with sulphate and hyposulphite of soda and small quantities of sulphide of iron (J. Löwe, *Jahresber.* 1857, 273.)

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Page 486.

*Ferrocyanide of Aluminum*,  $3\text{FeCy}, 2\text{Al}^3\text{Cy}^3$ . — Ferrocyanide of potassium added to the solution of an aluminum-salt, even when strongly acidulated, throws down a precipitate, which after ignition contains 44.89 p. c. alumina and 55.11 ferric oxide. (C. Tissier, *Compt. rend.* 45, 232.)

				Tessier. mean.
18 C .....	108.0	....	28.97	
9 N .....	126.0	....	33.80	
4 Al .....	54.8	....	14.70	14.87
3 Fe .....	84.0	....	22.53	22.36
<hr/>				
$3\text{FeCy}, 2\text{Al}^3\text{Cy}^3$ .....	372.8	....	100.00	

The precipitate is therefore a prussian blue in which the ferric cyanide is replaced by cyanide of aluminum. The analyses were made with precipitates obtained with various proportions of alumina-salt and yellow prussiate, the alumina-salt being, however, always in excess, and the liquid strongly acidulated. (Tissier.)

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Page 405.

*Decomposition of Cyanides by Hydriodic Ethers.* — Cyanide of mercury and *iodide of ethyl* decompose one another to a small amount when the mixture of their alcoholic solutions are evaporated, more completely when the same mixed solution is heated to  $120^\circ$  in a sealed tube. *Iodide of methyl* and *iodide of amyl* likewise decompose cyanide of mercury under the same circumstances — When dry cyanide of *potassium* is heated with alcohol and iodide of ethyl to  $100^\circ$  in a sealed tube, decomposition quickly takes place, with formation of iodide of potassium and cyanide of ethyl. Iodide of methyl acts in like manner; iodide of amyl only at  $140^\circ$  — Cyanide of *barium* acts like cyanide of potassium. — Cyanide of *zinc* does not appear to act on iodide of ethyl below  $140^\circ$  —  $160^\circ$ . — Iodide of ethyl is decomposed by cyanide of *silver* at  $160^\circ$  and by cyanide of *lead* at  $180^\circ$  with formation of metallic iodide and cyanide of ethyl. (Schlagdenhauffen, *Compt. rend.* 47, 740; 48, 228; *Ann. Pharm.* 109, 425.)

ADDITIONS TO VOL. VIII.

Page 10.

*Cuprosoferrocyanide of Potassium*,  $3\text{KCy}, 2\text{Cu}^2\text{Cy}, 2\text{FeCy} + 8\text{Aq}$ . — 1. A liquid consisting of cyanide of potassium and sulphate of copper containing iron, which had been used for coppering by electrolysis, and had stood for a long time in an imperfectly closed vessel, was found to have deposited brown-red octohedral crystals, resembling chrome-alum, and agreeing in composition with the above formula. — 2. The same salt was obtained in the form of a chocolate-coloured powder, by boiling cuprous cyanide  $\text{Cu}^2\text{Cy}$ , with solution of ferrocyanide of potassium, and leaving the filtered liquid to cool. (Bolley & Moldenhauer, *Ann. Pharm.* 106, 228.)

					Moldenhauer.	
					(1.)	(2.)
14 C	.....	84.0	....	15.04	.....	15.57
7 N	.....	98.0	....	17.56	.....	17.41
3 K	.....	117.6	....	21.03	.....	21.03
2 Fe	.....	56.0	....	10.11	.....	10.11
4 Cu	.....	126.7	....	22.64	.....	22.64
8 HO	.....	72.0	....	13.62	.....	13.24
$\text{K}^3\text{Fe}^2\text{Cu}^4\text{Cy}^7 + 8\text{Aq}$ ....					454.3	.... 100.00
					.....	100.00

The water in (1), was determined by loss.

(For Kühn's experiments on the action of ferrocyanide and ferricyanide of potassium on the oxides, sulphides and cyanides of copper, see *Ann. Pharm.* 87, 127, and *Zeitschr. Pharm.* 1859, 93.)

Page 17.

*Compounds of Cyanide of Mercury*. — The compounds containing 2 at. cyanide of mercury with 1 at. of another salt, such as  $2\text{HgCy}, \text{KI}$ ,  $2\text{HgCy}, \text{KCl}$ , &c., may be obtained, according to Geuther (*Ann. Pharm.* 106, 241), in well defined crystals, by dissolving 1 at. mercuric chloride, iodide, &c., in a solution of cyanide of mercury and potassium, sodium, &c. For this and other reasons, Geuther prefers representing them by the formulæ,  $\text{KCy}, \text{HgCy} + \text{KI}$ ,  $\text{KCy}, \text{HgCy} + \text{KCl}$ , &c. That the

whole of the cyanogen is not in combination with mercury, is considered by Geuther to be proved by the fact that these compounds are decomposed by arsenious and benzoic acids, with evolution of hydrocyanic acid. — The compound  $\text{KCy}, \text{HgCy} + \text{HgO}, \text{CrO}_3$ , or  $2\text{HgCy} + \text{KO}, \text{CrO}_3$  (viii, 23), may be obtained in fine yellow crystals by boiling basic mercuric chromate for some time, with an equivalent quantity of cyanide of mercury and potassium. The corresponding sulphate does not appear to exist.

The compound  $\text{K}^3\text{FeCy}^3 + 3\text{HgCy} + 4\text{HO}$  (viii, 25), may be obtained by agitating a moderately concentrated aqueous solution of ferricyanide of potassium with metallic mercury; a precipitate of sesquioxide of iron is first formed, mixed with mercury, and the yellowish filtrate yields the double salt by evaporation, in pale yellow rhombic tables. (J. Löwe, *Jahresber.* 1857, 273.)

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Page 29.

*Compounds of Cyanide of Silver.* — Cyanide of silver and potassium  $\text{KCy}, \text{AgCy}$ , crystallises, according to Glassford and Napier, in six-sided tables and rhombic prisms. From the experiments of Baup, however (*N. Ann. Chim. Phys.* 53, 462), it appears that when pure materials are used, the salt  $\text{KCy}, \text{AgCy}$ , crystallises on cooling in feathery laminæ, or by slow evaporation in six-sided tables, never in rhombic prisms. This salt requires for solution, 4 pts. of water at  $20^\circ$ , and 25 pts. of 85 p. c. alcohol, at the same temperature. It is not coloured by exposure to sunshine, and does not make stains on paper or on the skin. The cyanide of silver precipitated from it by nitric acid, is likewise unaltered by light.

*Cyanide of Silver and Sodium*,  $\text{NaCy}, \text{AgCy}$ , obtained by saturating a solution of cyanide of sodium with cyanide of silver, forms anhydrous laminated crystals. It dissolves in 5 pts. of water at  $20^\circ$ , and in 24 pts. of 85 p. c. alcohol, at the same temperature.

*Cyanide of Silver, Potassium, and Sodium*,  $2(\text{KCy}, \text{AgCy}) + \text{NaCy}, \text{AgCy}$ . Separates from the mother-liquor of cyanide of silver and potassium (the compound used for electroplating), when the cyanide of potassium used in its preparation contains cyanide of sodium. It is always anhydrous, and crystallises in short rhomboidal prisms (hitherto supposed to be cyanide of silver and potassium). It dissolves in 4.4 pts. of water at  $15^\circ$ , and in 22 pts. of alcohol at  $17^\circ$ . (Baup.)

The compound  $\text{AgCy}, \text{HgCy} + \text{HgO}, \text{NO}^5 + 4\text{Aq}$  or  $2\text{HgCy} + \text{AgO}, \text{NO}^5 + 4\text{Aq}$ , may be obtained by mixing mercuric nitrate with equivalent quantities of cyanide of silver and cyanide of mercury. It forms fine, long needles which melt above  $100^\circ$ , and then detonate. (Geuther, *loc. cit.*)

$\text{AgCy}, \text{HgCy} + \text{HgO}, \text{SO}^3 + \text{Aq}$  or  $2\text{HgCy} + \text{AgO}, \text{SO}^3 + \text{Aq}$ , is obtained in colourless crystals, by mixing the aqueous solution of 1 at. cyanide of mercury with 1 at. cyanide of silver and 1 at. neutral mercuric sulphate, boiling the mixture with addition of water till all the cyanide of silver and basic mercuric sulphate have disappeared, and evaporating. (Geuther.)

					Geuther.	
2 Hg	.....	200	....	47.96		
Ag	.....	108	....	25.90	..... 26.00	.... 26.50
O	.....	8	....	1.92		
SO <sup>3</sup>	.....	40	....	9.59	.....	.... 10.33
2 Cy	.....	52	....	12.47		
HO	.....	9	....	2.16	.....	.... 3.28
<hr/>						
AgHgCy <sup>2</sup> + HgO,SO <sup>3</sup> + Aq	.....	417	....	100.00		

If the materials are not boiled together long enough, a small quantity of a salt is obtained which crystallises out in needles before the preceding salt, and likewise contains cyanogen, mercury, silver, and sulphuric acid.

Page 60.

*Cyanide of Methyl with Terchloride of Phosphorus, C<sup>4</sup>H<sup>3</sup>N,PCl<sup>3</sup>.* — Produced by the action of pentachloride of phosphorus on acetamide. As the action is very violent, it is best to mix the chloride of phosphorus with an equal volume of sand. On distilling the mixture, a considerable carbonaceous residue is left, and the compound C<sup>4</sup>H<sup>3</sup>N,PCl<sup>3</sup>, passes over as a reddish pungent liquid, the greater part of which may be purified by several rectifications. Its formation cannot be represented by an equation: the copious residue which is left in the first distillation, shows that other compounds are formed at the same time. (W. Henke, *Ann. Pharm.* 106, 273.)

Colourless, mobile liquid which has a pungent odour, and exerts a strong irritating action on the respiratory organs. Boils at about 72°. The vapour density determined at 95° is 3.56; at 87°, it is 3.54, and at 148°, it is 2.4. It takes fire in contact with a spirit flame. (Henke.)

					Henke.	
4 C	.....	24	....	13.2	.....	13.3
3 H	.....	3	....	1.7	.....	1.7
N	.....	14	....	7.7	.....	7.4
P	.....	32	....	17.6	.....	17.5
3 Cl	.....	108	....	59.8	.....	60.1
<hr/>						
C <sup>4</sup> H <sup>3</sup> N,PCl <sup>3</sup>	.....	181	....	100.0	.....	100.0

	Vol.	Density.
C-vapour.....	4	..... 1.6640
H-gas .....	3	..... 0.2079
N-gas .....	1	..... 0.9706
P-vapour .....	$\frac{1}{2}$	..... 2.1770
Cl-gas .....	3	..... 7.3629
<hr/>		
Vap. of C <sup>4</sup> H <sup>3</sup> N,PCl <sup>3</sup> .....	4	..... 12.3824
	1	..... 3.0956

The unusual condensation to 4 volumes instead of 2, may perhaps be explained by supposing that at the temperature at which the vapour-density was determined, the compound splits up into cyanide of methyl and chloride of phosphorus, each of which occupies 2 volumes; just as if the density of vapour of water could be determined at a temperature at which it decomposes (near the melting point of platinum) without the decomposition being perceived, the molecule of water might be supposed to occupy three volumes instead of two, the oxygen occupying 1 vol. and the hydrogen 2 vol. (*vide* Kopp, *Ann. Pharm.* 105, 390).

This compound when kept in imperfectly closed vessels, soon deposits bulky white flakes, and then leaves, on distillation, a residue which gives off phosphuretted hydrogen when heated. It sinks in water, but decomposes after a few seconds with the greatest violence, yielding cyanide of methyl, hydrochloric acid, and phosphorous acid. (Hencke.)

The following compounds are obtained by direct union of cyanide of methyl with metallic chlorides. The combination is generally attended with so great a rise of temperature, that external cooling is necessary to prevent decomposition. Many of them crystallize well and distil without decomposition; but they are all instantly decomposed by water and alcohol, and cannot be recrystallized from ether. (W. Henke, *Ann. Pharm.* 106, 281.)

*Cyanide of Methyl with Chloride of Titanium*,  $C^4H^3N, TiCl^3$ . — Easily obtained by direct combination, which takes place without much evolution of heat. Forms white coherent crystalline crusts, which may be sublimed. Contains 17.93 to 18.30 p. c. titanium, the calculated quantity being 18.24 p. c. (Henke.)

*Cyanide of Methyl with Bichloride of Tin*,  $C^4H^3N, SnCl^2$ . — The combination of these substances is attended with evolution of heat, but not in sufficient amount to render it necessary to cool the vessel with ice. The compound is white, crystalline, and sublimes in arborescent frost-like crystalline formations. It gives by analysis, 33.25 and 34.28 p. c. tin, the formula requiring 34.11 p. c. (Henke.)

*Cyanide of Methyl with Pentachloride of Antimony*,  $C^4H^3N, SbCl^5$ . — The combination is attended with great evolution of heat, so that it is necessary to cool with ice. The crystals are white, imperfectly developed, and sublime without decomposition. By analysis, 37.09 and 38.80 p. c. antimony; by calculation 37.17 p. c. (Henke.)

*Cyanide of Methyl with Terchloride of Gold*,  $C^4H^3N, AuCl^3$ . — The two substances when brought together, form, without much evolution of heat, a brownish yellow powder which may be freed from excess of the cyanide, by pressure between paper. Gold, by analysis, 58.21 p. c.; by calculation, 37.10 p. c. (Henke.)

*Cyanide of Methyl and Mercury*,  $C^4H^3N, 4HgCy$ . — Finely pulverised cyanide of mercury absorbs cyanide of methyl with considerable rise of temperature, and if the cyanide of methyl is in excess, is converted into a crystalline mass, in which, after remaining for some months in a closed vessel, rectangular laminæ may be recognised. The crystals make a grating noise when crushed with a glass rod. They have a vitreous lustre, which they lose almost instantly on exposure to moist air, giving off cyanide of methyl at the same time and crumbling to a white powder. When dried over oil of vitriol, they give off the whole of the cyanide of methyl. The compound heated in a glass flask turns black, and yields a sublimate consisting of white crystals mixed with mercury. A sample freed from uncombined cyanide of methyl, by pressing it as quickly as possible between paper, yielded 74.4 p. c. mercury, the formula requiring 73.34 p. c. (O. Hesse, *Ann. Pharm.* 110, 202.)



## Page 80.

*Oxidation of Sulphocyanides.* — When an acidulated solution of a sulphocyanide is treated with permanganate of potash, the sulphur is oxidised to sulphuric acid. Aqueous hydrocyanic acid is not altered by permanganate of potash, if a stronger acid is present; but in neutral or alkaline solution, it quickly decolorises the permanganate. — The sulphur in sulphocyanides is very easily oxidised, as by peroxide of manganese or lead in presence of an acid; in the latter case, sulphate of lead is produced. The formation of sulphuric acid in these reactions is perhaps preceded by that of a cyanogen-compound containing less sulphur than sulphocyanogen.

When nitric acid is added to a sulphocyanide, the liquid assumes a deep red colour, which however is not permanent. Pure, colourless nitric acid exhibits this reaction only when gently heated, and in that case sulphuric acid is produced. Red nitrous vapours passed into the solution of a sulphocyanide produce the red colour immediately, but the formation of sulphuric acid appears to take place later. — Pure nitrous acid eliminated from the mixture of a nitrite and acetic acid, does not redden the solution of a sulphocyanide, probably because the acetic acid does not liberate the sulphocyanic acid; but a solution of free sulphocyanic acid is reddened by the vapours evolved from the mixture of a nitrite with acetic acid. — The reddening is produced by vapours of hyponitric acid  $\text{NO}^4$ , probably because that compound is resolved into  $\text{NO}^3$  and  $\text{NO}^5$ , the latter decomposing the sulphocyanide, and the former producing the reddening with the liberated sulphocyanic acid. The red colour is immediately destroyed by substances capable of uniting with the  $\text{NO}^3$ , viz. by metallic bases and even by alcohol. — The reddening is perhaps due to the formation of an unstable compound of nitrous acid, similar to the dark-coloured compound which is formed by the action of nitric oxide on ferrous salts. (E. A. Hadow, *Chem. Soc. Qu. J.* 11, 174.)

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## Page 83.

*Action of Hydriodic Ethers on Sulphocyanides.* — When iodide of methyl, ethyl, or amyl is heated with the sulphocyanide of an alkali-metal, earth-metal, or heavy metal in a sealed tube to between  $100^\circ$  and  $160^\circ$ , the iodine is transferred to the metal, and sulphocyanide of methyl, ethyl, or amyl is produced. With sulphocyanide of mercury only, a more complicated action appears to take place. Mixed with alcohol and heated in a sealed tube with iodide of ethyl, it yields a red deposit and a yellow liquid which contains but little sulphocyanide of ethyl, but when concentrated, deposits prismatic needles, probably a compound of sulphocyanide of ethyl with mercuric iodide. (Schlagdenhauffen, *N. Ann. Chim. Phys.* 56, 297.)

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## Page 125.

*Nitroprussides.* From the decomposition of these compounds by boiling with alkalis into nitrogen, ferric oxide, alkaline nitrite, and ferrocyanide, Gentele (*J. pr. Chem.* 74, 199) concludes that their rational formula is  $\text{NCy}^3, 2(\text{FeCyMO})$ .



*Hydride of Ethyl.* — The coefficients of absorption of hydride of ethyl  $C^4H^5H$  in water have been determined by Schickendantz (*Ann. Pharm.* 109, 116); they differ but little from those of the isomeric compound methyl, as determined by Bunsen (*Bunsen's Gasometry, translated by Roscoe*, p. 288). — The following table exhibits the values.

Temp.	Absorption co-efficients.		Temp.	Absorption co-efficient	
	Hydrate of Ethyl.	Methyl.		Hydride of Ethyl.	Methyl.
0°	0·0946	0·0871	13°	0·0595	0·0541
1	0·0911	0·0838	14	0·0574	0·0524
2	0·0877	0·0807	15	0·0557	0·0508
3	0·0845	0·0777	16	0·0541	0·0493
4	0·0814	0·0748	17	0·0536	0·0480
5	0·0785	0·0720	18	0·0513	0·0468
6	0·0756	0·0693	19	0·0501	0·0457
7	0·0729	0·0668	20	0·0490	0·0447
8	0·0703	0·0644	21	0·0480	
9	0·0678	0·0621	22	0·0473	
10	0·0655	0·0599	23	0·0465	
11	0·0633	0·0578	24	0·0459	
12	0·0612	0·0559			

*Ethylated Sulphuric Acid.* — According to Jacquemin and Lies-Bodard (*Comp. rend.* 46, 990), 1 at. strong sulphuric acid takes up 1 at. ether in such manner that the odour of the ether is no longer perceptible; but the ether is set free on heating the liquid or on mixing it with water.

*Preparation of Alcohol.* — A method of preparing alcohol from man-gold wurzel, so as to convert, not only the sugar in the plant, but also the starch, gum, cellulose, &c., into alcohol, has been described by F. Weil. (*Dingl. Pol. J.* 150, 421).

For the defuselization of alcohol, Kletzinsky (*Dengl. Pol. J.* 148, 150), recommends distilling it over soda-soap; Breton (*Dengl. Pol. J.* 150, 424) agitates the spirit with a few drops of olive-oil, which unites with the fusel-oil, and then decants the liquid; for operations on the large scale, he filters the spirit through pumice-stone soaked in oil; the fusel-oil may afterwards be separated from the pumice-stone by distillation.

On the preparation of absolute alcohol, see Rieckher (*N. Jahrb. Pharm.* 10, 308), and on the alteration in the composition of hydrated alcohol by spontaneous evaporation, whereby a liquid comparatively rich in alcohol passes off, and a weaker spirit remains, see A. Vogel, jun. (*Wien. Akad. Ber.* 30, 261 ; *Chem. Centr.* 1858, 712).

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Page 202.

*Decomposition of Alcohol by the Electric Spark.* — When the sparks from an induction coil are passed through liquid alcohol, the alcohol soon acquires an acid reaction, deposits black flocks, gives off gas, and forms a resinous substance. The decomposition and the evolution of gas are considerably accelerated by addition of a small quantity of potash. The evolved gas is similar in composition to that which is produced in the decomposition of alcohol by heat, but appears to be the result of a more thorough decomposition. When it is placed in contact with ammoniacal solution of cuprous chloride, that liquid absorbs carbonic oxide from it, and deposits a dull copper-coloured substance which becomes brown when dry, and explodes with appearance of light when heated above  $100^{\circ}$ , or struck with the hammer ; heated with hydrochloric acid, it gives off a gas which burns and yields carbonic acid. With an ammoniacal solution of chloride of silver, the gas forms a white precipitate which becomes yellow and then brick-red by exposure to light, turns grey when dry, and explodes like the copper compound. The substance to which these compounds owe their explosive property is present in small quantity only ; it is not removed by strong sulphuric acid, and it appears to be likewise present in the gas produced by passing the vapour of alcohol through a strongly ignited tube, inasmuch as that gas forms with ammoniacal solution of dichloride of copper or chloride of silver, detonating compounds resembling those above mentioned (A. Quet, *Compt. rend* 46, 903 ; *Ann. Pharm.* 108, 116).

2. When electric sparks are passed for a long time through the vapour of alcohol or ether, gas is eliminated in considerable quantity, and the alcohol is at length completely decomposed ; no water is formed, and the solid residue consists only of a trace of resin and a small quantity of charcoal. The gas does not contain ethylene, but it is absorbed by bromine, forming a colourless liquid which has a sweet taste, smells like chloroform, and is decomposed by fractional distillation into two liquids, one of which passes over between  $135^{\circ}$  and  $140^{\circ}$  ; and the other at about  $240^{\circ}$ .

The liquid which passes over between  $135^{\circ}$  and  $140^{\circ}$ , does not solidify at  $15^{\circ}$  ; it is oily to the touch, has a density of 2.347 at  $0^{\circ}$ , and gives by analysis numbers agreeing with the formula  $C^6H^6Br^3$  ; it is therefore isomeric with terbromide of allyl and bromide of bromopropylene :

				Perrot.		
				From alcohol.	From ether.	
6 C .....	36	...	12.81	..... 12.74	...	12.73
5 H .....	5	...	1.78	..... 2.20	...	2.03
3 Br.....	240	...	85.41	..... 85.60	...	85.63
$C^6H^6Br^3$ .....	281	...	100.00	..... 100.54	...	100.39

The liquid which passes over towards  $240^{\circ}$  likewise retains its fluidity at  $15^{\circ}$ ; it has a density of 2.966 at  $0^{\circ}$ , and burns with a reddish fuliginous flame. It gives by analysis nearly constant numbers which however do not admit of reduction to any simple formula.

		<i>From alcohol.</i>				<i>From ether.</i>		
C	.....	7.79	....	7.92	....	7.79	.....	8.27
H	.....	0.92	....	0.92	....	1.23	.....	1.16
Br	.....	91.32	....		....	90.65	.....	89.68
		100.03	....		....	99.67	.....	99.11

These are the only bromine-compounds which can be obtained from the gas resulting from the decomposition of alcohol or ether vapour by the electric spark (Perrot, *Compt. rend.* 46, 180; 47, 351, *Ann. Pharm.* 108, 113.)

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Page 220.

*Decomposition of Alcohol by Aqua regia.* — When aqua regia prepared from pure hydrochloric and the strongest nitric acid, is added to an equal volume of alcohol of  $36^{\circ}$ , bubbles of vapour begin to form after 10 or 15 minutes and the temperature rises till the liquid boils. Aldehyde, nitric ether, formic ether, chloral, and formic acid, then distil over, perhaps also chloroform (chloride of ethyl was not observed), and nitrous and nitric oxide are given off. The residual liquid yields by distillation, alcohol, acetic acid, acetic ether, oxalic ether, acetal or an analogous liquid boiling at  $102^{\circ}$ ; and the residue which is still left, contains oxalic, nitric, hydrochloric, and oxyglycolic (?) acid, and peculiar resinifying substances not yet examined. (H. Bonnet, *Compt. rend.* 45, 386).

On the action of chlorine on hydrated alcohol, see *chlorinated acetals* (additions to to vol. ix).

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Page 222—253. .

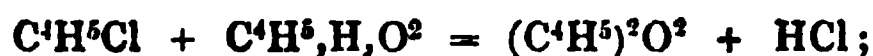
### Etherification.

A. REYNOSO. *N. Ann. Chim. Phys.* 48, 385; *Ann. Pharm.* 101, 100.

The following experiments were made by heating the reacting substances in sealed glass tubes.

*Action of Hydrochloric acid upon Alcohol.* — When alcohol is heated to  $100^{\circ}$  with excess of hydrochloric acid, nothing but chloride of ethyl is formed, as when the mixture is distilled under the ordinary atmospheric pressure; but when a mixture of hydrochloric acid with a larger excess of alcohol, either hydrated or anhydrous, is heated for seven or eight hours to  $240^{\circ}$ , a different action takes place, and two layers of liquid are

formed on cooling, the upper containing oxide and chloride of ethyl, and the lower water and hydrochloric acid, with small quantities of ether and chloride of ethyl. The quantity of ether formed increases with the excess of alcohol; and by continuing the action long enough, a considerable quantity of alcohol may be converted into ether by the action of a small quantity of hydrochloric acid. The same transformation takes place, though more slowly, at lower temperatures, even at 100°. The formation of ether by the action of hydrochloric acid upon alcohol, probably takes place in the same manner as by the action of metallic chlorides, chloride of ethyl being first formed and then acting upon the rest of the alcohol so as to form ether and hydrochloric acid;



and the hydrochloric acid thus reproduced, forms a fresh quantity of chloride of ethyl; and so the process goes on till all the alcohol is converted into ether.

*Hydrobromic and Hydriodic Acid* act upon alcohol in the same manner as hydrochloric acid. The aqueous solutions of these acids heated with excess of alcohol to 200° for ten hours, yield considerable quantities of ether, together with bromide or iodide of ethyl.

The action of *hydriodic* or *hydrobromic acid* upon *ether* produces bromide or iodide of ethyl; when ether has been heated with excess of the aqueous solution of either of these acids, the tube contains two layers, the upper consisting of iodide or bromide of ethyl with a little undecomposed ether, and the lower of water, hydriodic or hydrobromic acid, and ether.

*Action of Mercuric Oxide on Bromide and Iodide of Ethyl.* — After a mixture of equal parts of bromide of ethyl and dry mercuric oxide has been heated for 15 hours, the oxide is found to be converted into a white powder consisting of mercurous and mercuric bromide. The liquid remaining in the tube consists of ether, bromide of ethyl, and acetate of ethyl, and moreover contains in solution, a crystallizable substance which blackens when heated, and yields a sublimate of bromide of mercury; no gas is evolved.

When dry mercuric oxide was heated with *iodide of ethyl* to 260° for four hours, an energetic action took place; a blackened mass was formed containing a small quantity of reduced mercury together with a very mobile liquid; and at the same time, such a quantity of gas was formed that the tube exploded on being opened; for this reason nothing could be ascertained respecting the products of the decomposition, excepting that a portion of the iodine was set free. — When dry mercuric oxide was heated with iodide of ethyl for six hours to 100°, iodide of mercury was formed, together with ether, a small quantity of olefiant gas and a trace of acetate of ethyl (part of the iodide of ethyl remained undecomposed). — When a tube containing iodide of ethyl and dry mercuric oxide was exposed to the sun's rays for 17 days at the atmospheric temperature, iodide of mercury was formed, and on opening the tube, a large quantity of gas was given off, a small quantity of ether and acetate of ethyl remaining behind. The formation of acetate of ethyl is ascribed by Reynoso to a secondary action of the mercuric oxide on the ether.

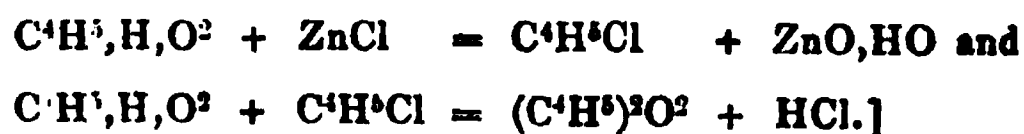
*Action of Water on Bromide and Iodide of Ethyl.* — When bromide of ethyl is heated to 200° for 12 hours with an equal weight or more of water, the products formed are common ether, olefiant gas, hydrobromic acid, and the so-called oils of wine. Part of the bromide of ethyl remains undecomposed, only a small portion however, if the quantity of water amounts to three times that of the bromide of ethyl or more.

That iodide of ethyl is decomposed by water at 150°, with formation of ether, was previously shown by Frankland. According to Reynoso, the decomposition of iodide of ethyl by water is exactly similar to that of the bromide.

*Action of Bromide and Iodide of Ethyl upon Alcohol.* — When a mixture of alcohol and bromide of ethyl is heated to 200° for 8 hours, the alcohol disappears and ether is formed, together with hydrobromic acid; in this manner, small quantities of bromide of ethyl may convert large quantities of alcohol into ether; a certain quantity of bromide of ethyl always remains undecomposed. Iodide of ethyl acts upon alcohol in the same manner, but less quickly. Heated with aqueous alcohol, it likewise forms ether in greater or smaller quantity, according as the alcohol is more or less concentrated.

*Action of Metallic Chlorides, Bromides, and Iodides on Alcohol.* — The experiments were made, by heating about equal weights (15 grm.) of the metallic chloride and alcohol of 98 per cent. in sealed tubes to 240° for 7 or 8 hours. — Crystallised *chloride of manganese* etherifies alcohol completely, without itself suffering decomposition. The same action is exerted, though less completely, by the chlorides of *cobalt* and *cadmium*. — *Chloride of nickel* etherifies alcohol partially, but a portion of the chloride is at the same time converted into insoluble, greenish-yellow, basic chloride. The conversion of alcohol into ether by the preceding chlorides is not attended with any blackening of the contents of the tube, neither does any gas escape when the tube is opened. Crystallised *protochloride of iron* etherifies alcohol completely, without blackening; a small quantity of gas is however produced, and the solid mass remaining in the tube consists of protochloride of iron and a radio-crystalline substance which is insoluble in water, and is converted by boiling water into a black powder. — Crystallised *protochloride of tin* likewise etherifies alcohol completely, and at the termination of the experiment, a layer of ether is found in the tube, floating upon a milky liquid; gas escapes on opening the tube, and the protochloride of tin exhibits marks of partial decomposition. — *Mercuric chloride* heated with alcohol to between 200° and 240° decomposes and blackens, and on opening the tube, a large quantity of gas escapes; ether is also formed. — When *hydrochlorate of morphine* or of *cinchonine* is heated with alcohol to 200°, the mixture blackens, but no gas escapes on opening the tube; the liquid contains small quantities of ether.

With regard to the manner in which metallic chlorides convert alcohol into ether, Reynoso considers it most probable that the etherification is effected by a portion of hydrochloric acid liberated from the metallic chloride, which then, on cooling, recombines with the oxychloride or oxide formed in the first instance, supposing that this latter compound has not been rendered insoluble in the acid by the high temperature. [Is not the following more probable?



*Bromide and Iodide of Cadmium* act upon alcohol at  $240^{\circ}$  in the same manner as the chloride, forming a small quantity of ether; *mercuric bromide* acts also like the chloride. *Mercuric iodide* (prepared by precipitation and then washed and dried) heated with absolute alcohol to  $240^{\circ}$  for 4 or 5 hours converts the greater part of it into ether, without itself undergoing alteration. At  $300^{\circ}$  the contents of the tube blacken, and a very large quantity of gas is formed.

*Action of Sulphuric Acid upon Alcohol.* — The results obtained by heating together sulphuric acid and alcohol in sealed tubes, vary greatly with the strength of the acid, the temperature, the duration of the experiment, and the proportions of acid and alcohol used. Experiments with sulphuric acid of various strengths, containing from 81.6 to 0.5 per cent. of anhydrous acid and heated with alcohol in various proportions to between  $100^{\circ}$  and  $200^{\circ}$ , showed that the temperature must be raised higher and the action continued longer, in proportion as the acid is more dilute. The products which may be formed are olefiant gas, the oils of wine, ethylsulphuric (sulphovinic) acid, and ether, frequently also sulphurous acid. — With a large excess of alcohol, ether and ethylsulphuric acid are generally the only products; when the sulphuric acid is in large excess, the mixture strongly heated, or the action continued for a considerable time at a lower temperature, only a small quantity of ether is produced. — At high temperatures, olefiant gas is found among the products of decomposition; this gas is never formed between  $100^{\circ}$  and  $120^{\circ}$ , but sulphurous acid may be formed within these limits of temperature. — The quantity of ether formed is greatest at all temperatures when the alcohol is in large excess in proportion to the sulphuric acid. With acid of strength comprised between the limits above-mentioned, the conversion of alcohol into ether takes place at all temperatures between  $100^{\circ}$  and  $200^{\circ}$ , provided the proportions of acid and alcohol are properly chosen, and the duration of the experiment is properly regulated according to the temperature. The formation of olefiant gas does not always take place at the temperatures at which ether is formed, but only at somewhat higher temperatures; olefiant gas is formed even with dilute sulphuric acid, if the temperature is high enough, the action continued long enough, and the acid in large excess in proportion to the alcohol. In most of the experiments on the action of sulphuric acid upon alcohol, ethylsulphuric acid was also formed in greater or smaller quantity, excepting when very dilute sulphuric acid was used; when ethylsulphuric acid was formed, its quantity appeared to be in direct proportion to that of the sulphuric acid used.

*Action of Sulphates upon Alcohol.* — The crystallised salts were heated in sealed tubes with an equal weight of .98 per cent. alcohol. The crystallised sulphates of *magnesia*, *manganous oxide*, *ferrous oxide*, *zinc-oxide*, *cadmium-oxide*, *cobalt-oxide*, and *uranic oxide* (especially the last) convert small quantities of alcohol and ether at  $240^{\circ}$ , without themselves undergoing any alteration or giving rise to the formation of secondary products. Alcohol is likewise etherified at  $240^{\circ}$  by sulphate of *nickel*, which however is at the same time partially reduced to a basic salt; also by *cupric sulphate*, a portion of that salt being at the same time reduced to metallic copper, and a considerable quantity of gas evolved. — *Sulphate of alumina* etherifies alcohol completely between  $200^{\circ}$  and  $240^{\circ}$ , without simultaneous formation of gas, and is thereby partially reduced to insoluble basic salt. When the sulphates of *ammonia*, *potash*, *soda*,



and *lime* are heated with alcohol to  $240^{\circ}$ , no definite result is obtained with reference to etherification. *Ferric sulphate* heated with alcohol to  $240^{\circ}$  forms ether, and likewise a large quantity of gas (containing sulphurous acid), and is itself decomposed. — *Sulphate of alumina and potash* etherifies alcohol completely at  $200^{\circ}$ , without evolution of gas, but with formation of a certain quantity of basic sulphate of alumina; etherification takes place also at  $240^{\circ}$ , but is accompanied by formation of gas and of a larger quantity of the basic salt. — *Sulphate of alumina and ammonia* etherifies alcohol completely between  $200^{\circ}$  and  $240^{\circ}$ , without formation of gases, but with partial formation of basic sulphate of alumina. When *potassio-ferric sulphate* is heated with alcohol to  $240^{\circ}$ , the alcohol is likewise wholly converted into ether, but the change is attended with the evolution of a large quantity of gas and partial formation of basic ferric sulphate. — *Potassio-chromic sulphate* etherifies alcohol completely at  $240^{\circ}$  and even at  $200^{\circ}$ , without formation of gas; after heating to  $200^{\circ}$ , the solid part of the contents of the tube dissolves completely in water; after heating to  $240^{\circ}$ , a small quantity of greenish residue is obtained insoluble in water.

Reynoso explains the action of sulphates upon alcohol by supposing that a portion of the sulphuric acid is set free and forms ethyl-sulphuric acid, which, acting upon the rest of the alcohol, or being decomposed by heat, forms ether and reproduces sulphuric acid (compare page 237). This view is in accordance with the fact that those sulphates, viz.: the sulphates of sesquioxides, which most readily give up part of their acid when heated, are likewise those which etherify alcohol with the greatest facility.

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Page 237.

*Formation of Oil of Wine, &c.* (Blondeau, *N. J. Pharm.*, xxix, 249, 344, 424).— When a mixture of 2 pts. alcohol, 3 pts. oil of vitriol, and 1 pt. water is distilled, the liquid which passes over above  $160^{\circ}$  separates into three layers, the lowest of which is the so-called *heavy oil of wine*, consisting, according to Blondeau, of sulphetheric acid,  $C^4H^5O^2, S^2O^6$  (x, 518), while the middle layer consists of aqueous sulphuric acid, and the uppermost of the so-called *light oil of wine*, which, by fractional distillation, yields an oily liquid containing equal numbers of atoms of carbon and hydrogen, boiling at  $28^{\circ}$ , having a density of 0.621 in the liquid state, and a vapour density of 3.9. This liquid, *ethene*, may also be obtained by treating pure ether with potassium and distilling the product,  $C^4H^4KO$ , with dilute sulphuric acid. — Ethene combines with sulphuric acid, forming *ethene-sulphuric acid*, the salts of which are composed of  $C^4H^3S^2O^5, MO$ . This salt is formed in a mixture of alcohol and sulphuric acid by heating it to  $170^{\circ}$ , whereas at  $140^{\circ}$  the same mixture yields sulphovinic acid, and at  $160^{\circ}$  sulphetheric acid (x, 518). The oil of wine which passes over in the distillation of sulphovinate of lime consists of butyl-sulphuric acid. [These statements of Blondeau are at complete variance with the results of former observers. (p. 175 of this volume). The subject requires further examination].

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Page 255.

*Ethylate of Sodium.* — According to Geuther (*Ann. Pharm.* 109, 73), ethylate of sodium,  $C^4H^5NaO^2$ , is decomposed by carbonic oxide at  $100^{\circ}$ , yielding formiate of soda. To explain this result, Geuther supposes that the ethylate of soda is first resolved into ethylene and hydrate of soda, the latter being then converted into formiate by the carbonic oxide

(x. 490): no evolution of ethylene gas was however observed. Wanklyn (*Ann. Pharm.* 110, 111), supposes that the production of formiate of soda in Geuther's experiment was due to the presence of hydrate of soda in the ethylate of sodium used; according to Wanklyn's observation, carbonic acid does not act upon ethylate of sodium at  $100^{\circ}$ , neither is any ethylene gas set free.

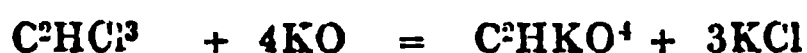
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Page 266.

*Action of Alcoholic Potash on Chlorine-compounds.* — The action of alcoholic potash on organic chlorides, bromides, &c. is generally regarded as consisting merely in an interchange between the chlorine of the organic compound and the oxygen of the potash, the alcohol acting merely as a solvent, and the more energetic action of alcoholic potash on these compounds being due to the circumstance that both the potash and the organic compound are dissolved in the same solvent: thus—



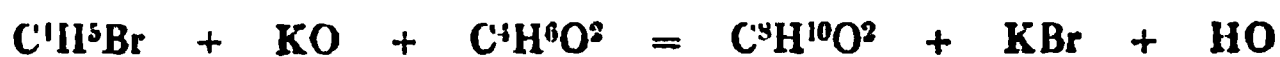
and :



Berthelot has, however, shown that this is not the case, but rather that the alcohol plays an essential part in the reaction. He had previously shown (ix, 172) that, in the formation of oxide of ethyl by the action of alcoholic potash on bromide of ethyl, the quantity of ether obtained is nearly twice as great as it should be according to the equation:



and that it really takes place as shown by the more complex equation :



And he has lately demonstrated that in the action of alcoholic potash on bichloride of carbon and chloroform, the alcohol itself suffers decomposition. When a mixture of potash, alcohol and bichloride of carbon or chloroform is heated to  $100^{\circ}$  for a week in sealed tubes, a certain quantity of pure ethylene gas is produced, [according to Hermann (x, 499), bromoform treated with alcoholic potash yields a mixture of ethylene and carbonic oxide]; and under the same circumstances, a mixture of alcoholic potash and sesquichloride of carbon  $C^4Cl^6$ , or protochloride of carbon  $C^4Cl^4$  yields ethylene and hydrogen gases. That these reactions are attended with further and still unexplained decompositions, appears from the fact that not only is carbonic acid  $C^3O^4$  produced from  $C^2Cl^4$ , formic acid  $C^2HO^3$ , HO from chloroform  $C^2HCl^3$ , and oxalic acid  $C^4O^6, 2HO$  from sesquichloride of carbon  $C^4Cl^6$ , and that generally compounds are formed containing oxygen in place of the carbon of the original substance,—but there are also formed a number of liquid products and insoluble humus-like substances similar to those which are produced by the action of alkalis on grape-sugar. (Berthelot, *N. Ann. Chim. Phys.* 54, 87; *Ann. Pharm.* 109, 118).



*Alcoholate of Baryta.* — According to Berthelot (*N. Ann. Chim. Phys.* 46, 180; *Ann. Pharm.* 98, 180), the compound originally obtained by Kuhlmann (viii, 266), by the action of anhydrous baryta on absolute alcohol is  $\text{BaO}, \text{C}^4\text{H}^6\text{O}^3$ , and therefore homologous with the compound  $\text{BaO}, \text{C}^3\text{H}^4\text{O}^3$ , which Dumas & Peligot obtained by the action of anhydrous baryta on anhydrous methylic alcohol (vii, 267).

### Glycol and its Derivatives.

- A. WURTZ. *N. Ann. Chim. Phys.* 55, 400. See also, Memoirs cited at page 501, vol. xii, and in addition; *Compt. rend.* 45, 228, 47, 346; *Ann. Pharm.* 104, 174; 108, 84.—New researches on oxide of Ethylene; *Bulletin de la Société Chimique de Paris*, 1, 79.  
 E. ATKINSON. *Phil. Mag.* [4] 16, 433; *Ann. Pharm.* 109, 232.  
 H. DEBUS. *Ann. Pharm.* 110, 216.  
 LOURENÇO. *Bull. Sec. Chim. de Paris*, 1, 77.  
 MAXWELL SIMPSON. *Proc. Roy. Soc.* 9, 725; 10, 114.

*Preparation of Glycol.* — Wurtz obtained glycol by decomposing the biacetate of ethylene with potash, the biacetate being obtained by the action of iodide of ethylene on acetate of silver. For the preparation of the biacetate, he now recommends the use of bromide of ethylene instead of the iodide — the former being more easily obtained, and having a lower combining number.

Atkinson prepares glycol by the action of potash or baryta on monoacetate of ethylene  $\left. \begin{matrix} \text{C}^4\text{H}^4 \\ \text{C}^4\text{H}^3\text{O}^2, \text{H} \end{matrix} \right\} \text{O}^4$ , which is obtained by heating bromide of ethylene with acetate of potash. This reaction is more regular and less complicated with secondary decompositions than that of acetate of silver on the bromide or iodide of ethylene, and moreover the use of acetate of potash is much more economical than that of acetate of silver. — According to Debus, the quantity of glycol obtained by decomposing the monoacetate with potash is only about half the calculated quantity, the loss apparently arising from the formation of a compound which is but slowly resolved by heat into glycol and acetate of potash. He therefore recommends the following process: The monoacetate of ethylene mixed with an equal volume of water is exposed for 12 or 16 hours in a strong, well-corked flask to the temperature of boiling water, whereby it is for the most part resolved into acetic acid and glycol. On distilling the contents of the flask, water and acetic acid pass over below  $150^\circ$ , glycol mixed with a considerable quantity of the undecomposed acetate between  $150^\circ$  and  $190^\circ$ , and above  $190^\circ$ , glycol containing a comparatively small portion (about 15 p. c.) of the acetate. The portion boiling between  $150^\circ$  and  $190^\circ$  is again heated with water in a close vessel; the portion of the product which distils above  $190^\circ$  is mixed with the former portion boiling at that temperature; the whole is distilled with a quantity of solid potash, just sufficient to neutralise the acetic acid; and the liquid which passes over at  $245^\circ$  is rectified. Glycol is thus obtained boiling at  $196^\circ$ .

*Oxidation of Glycol.* — 1. When glycol diluted with four times its volume of water is placed in a tall glass vessel, *fuming nitric acid* poured

in through a long tube-funnel so as to form a layer at the bottom of the vessel, the whole heated to about  $30^{\circ}$ , and the acid liquid evaporated to a syrup, the residue is found to contain glycolic and oxalic acids, as previously observed by Wurtz (xii, 502), likewise glyoxylic acid (xii, 505) and a body which exhibits some of the properties of glyoxal (xii, 503). — 2. Glycol heated with *hydrate of potash* recently fused and pulverised yields a large quantity of hydrogen, and a residue containing oxalate of potash, together with a small quantity of carbonate, and, perhaps, of glycolate. The principal part of the reaction is represented by the equation:



*Action of Pentachloride of Phosphorus on Glycol.* — When pentachloride of phosphorus is gradually added to glycol, a violent action takes place, rendering it necessary to surround the vessel with a frigorific mixture. On continuing to add the perchloride, the mixture thickens at first, but ultimately becomes quite fluid when 2 at.  $\text{PCl}^5$  have been added to 1 at. glycol. Towards the end of the operation, the action becomes less vivid, and the freezing mixture must be removed. On distilling the product, a mixture of oxychloride of phosphorus and chloride of ethylene passes over below  $100^{\circ}$ , and nearly pure oxychloride above that temperature. On agitating the former portion with water, the oxychloride of phosphorus is decomposed, and an oily liquid remains, which, after being dehydrated by chloride of calcium, distils at  $84^{\circ}$ , and exhibits the properties and composition of *chloride of ethylene*  $\text{C}^4\text{H}^4\text{Cl}^2$  (carbon 24.24 p. c. hydrogen 4.27:—by calculation, 24.24 and 4.04). (Wurtz). — The reaction is represented by the equation:



*Action of Chloride of Zinc on Glycol.* — Anhydrous chloride of zinc exerts a dehydrating action on glycol, abstracting 2 at. water and leaving *aldehyde*:



When 3 pts. of chloride of zinc are heated with 1 pt. of glycol in a flask provided with a distillation-tube and immersed in an oil-bath, a brisk action takes place at about  $250^{\circ}$ , and vapours are evolved, which, when condensed in a well cooled receiver, yield two layers of liquid, the upper of which is oily and consists of hydrocarbons, while the lower, which is watery, is a mixture of aldehyde and another volatile liquid, apparently isomeric with it. On subjecting the mixture to fractional distillation, a liquid passes over below  $20^{\circ}$ , which, when dissolved in twice its volume of ether and saturated with ammonia, yields crystals of aldehyde-ammonia. The other liquid which distils above  $21^{\circ}$  is soluble in water, insoluble in a concentrated solution of chloride of calcium, has a very strong odour and hot taste, and distils between  $70^{\circ}$  and  $100^{\circ}$ . A portion which distilled at about  $80^{\circ}$  gave by analysis 54.7 p. c. C and 9.5 H, showing that it is isomeric with aldehyde (54.5 p. c. C and 9.0 H). — Another portion distilling between  $90^{\circ}$  and  $100^{\circ}$  gave 57.4 C and 9.6 H. It was probably the same liquid mixed with a small quantity of the hydrocarbons above mentioned.

The oily liquid floating on the watery layer consists chiefly of a mixture of hydrocarbons richer in carbon than ethylene. A portion boiling

at about  $200^{\circ}$  gave 84.4 p. c. C., 10.6 H and 5.0 O. These hydrocarbons probably result from a more complete dehydration of the glycol. Supposing  $\text{H}^4\text{O}^4$  to be abstracted from that compound, there would remain  $\text{C}^4\text{H}^2$ , a hydrocarbon which could not perhaps exist by itself, but would be resolved into other hydrocarbons in which the carbon would be the predominating element. (Wurtz.)

*Terchloride of Antimony* dissolves abundantly in glycol; and the liquid yields, by distillation, vapours of hydrochloric acid, and an acid liquid mixed with chloride of antimony; the residue blackens considerably: aldehyde was not found among the products. (Wurtz.)

*Action of Sodium on Glycol.* — Glycol is energetically attacked by sodium, with evolution of hydrogen, and formation of a white crystalline substance, which is *monosodic glycol*  $\left. \begin{matrix} \text{C}^4\text{H}^4 \\ \text{NaH} \end{matrix} \right\} \text{O}^4$ , and this product fused with excess of sodium again gives off hydrogen, and is converted, slowly and with difficulty, into *bisodic glycol*  $\text{C}^4\text{H}^4, \text{Na}^2, \text{O}^4$ .

Bisodic glycol, heated with bromide of ethylene, in a flask communicating with a receiver, surrounded with a freezing mixture, yields *bromide of aldehydene*  $\text{C}^4\text{H}^3\text{Br}$ , together with glycol and bromide of sodium:



Monosodic glycol, heated in a sealed tube with bromide of aldehydene, yields olefiant gas and glycol, together with bromide of sodium and a small quantity of a soda-salt soluble in alcohol, and yielding when decomposed by sulphuric acid, an acid which smells like acetic acid, but reduces silver-salts. (Wurtz.)

## Glycolic Ethers.

*Oxide of Ethylene.*  $\text{C}^2\text{H}^4\text{O}^2$ . — When glycolic chlorhydrin  $\text{C}^2\text{H}^3\text{ClO}^2$  is treated with aqueous potash, chloride of potassium is formed and oxide of ethylene is given off in the form of a vapour, which may be condensed in a receiver surrounded with a freezing mixture and containing a few lumps of chloride of calcium, over which the product may be afterwards rectified:



Oxide of ethylene is a transparent, colourless liquid, which boils at  $13.5^{\circ}$  under a pressure of 746.5 m.m. (Aldehyde, with which it is isomeric, boils at  $21^{\circ}$ .) Vapour-density 1.422.

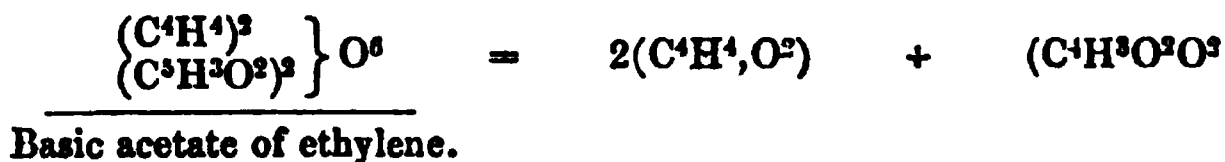
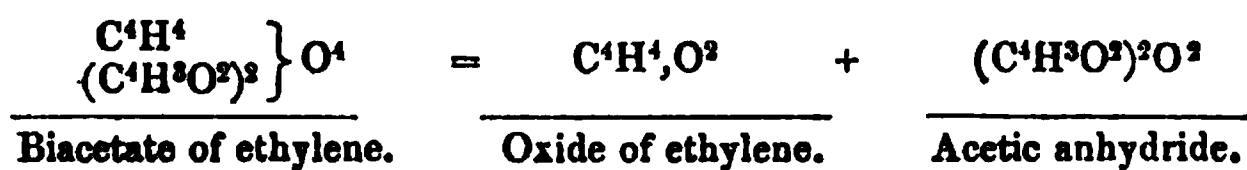
Wurtz.										Vol.		Density.	
mean.													
4 C	....	24	....	54.54	....	54.55	.....	C-vapour	....	4	....	1.6640	
4 H	...	4	....	9.09	....	9.14	.....	H-gas	....	4	....	0.2572	
2 O	....	16	....	36.37	....	36.31	.....	O-gas	....	1	....	1.1093	
<hr/>													
$\text{C}^2\text{H}^4\text{O}^2$	....	44	....	100.00	....	100.00	.....	Vap. of $\text{C}^2\text{H}^4\text{O}^2$		2	....	3.0305	
										1	....	1.5152	

Oxide of ethylene is decomposed by pentachloride of phosphorus, yielding chloride of ethylene and oxychloride of phosphorus:



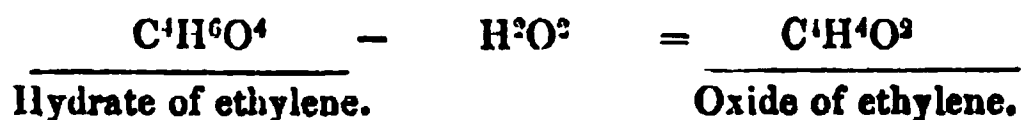
The compound  $\text{C}^4\text{H}^4\text{Cl}^2$  thus obtained has the same boiling point ( $84^\circ$ ) as ordinary Dutch liquid.

Oxide of ethylene does not, like aldehyde, form a crystalline compound with ammonia; on the contrary, it exhibits the properties of a base. It unites directly with water, and reproduces glycol. By heating it with water for several days in a strong sealed tube, a sweetish liquid is obtained, which, by distillation, yields glycol, and afterwards at  $256^\circ$ , a compound  $\text{C}^6\text{H}^{10}\text{O}^6$ , intermediate in composition between oxide of ethylene and glycol. — Oxide of ethylene unites directly with and neutralises hydrochloric acid, forming *glycolic chlorhydrin*  $\text{C}^4\text{H}^5\text{ClO}^2 = \text{C}^4\text{H}^4\text{O}^2, \text{HCl}$ . — It also unites with acetic acid or acetic anhydride, forming *biacetate of ethylene*  $\text{C}^4\text{H}^4, (\text{C}^4\text{H}^3\text{O}^2)^2, \text{O}^6$  boiling at  $185^\circ$ , and *basic acetate of ethylene*  $(\text{C}^4\text{H}^4)^2, (\text{C}^4\text{H}^3\text{O}^2)^2, \text{O}^6$ , which boils at a much higher temperature. The combination takes place slowly at ordinary, rapidly at higher temperatures. The formation of these two compounds from acetic anhydride is represented by the equations:



When acetic acid is used instead of the anhydride, the formation of these compounds is attended with elimination of water.

The preceding reactions show that oxide of ethylene is the true ether or anhydride of glycol, and consequently that the anhydrides of biatomic alcohols contain the same number of carbon-atoms as the alcohols themselves, and are derived from them by elimination of water, resembling in this respect, the anhydrides of bibasic acids: *e.g.*,



The compound  $\frac{\text{C}^4\text{H}^4}{\text{C}^4\text{H}^4} \left\} \text{O}^4$ , which would stand to glycol  $\frac{\text{C}^4\text{H}^4}{\text{H}^2} \left\} \text{O}^4$ , in the same relation as common ether  $\frac{\text{C}^4\text{H}^6}{\text{C}^4\text{H}^5} \left\} \text{O}^2$  to alcohol  $\frac{\text{C}^4\text{H}^5}{\text{H}} \left\} \text{O}^2$ , does not appear to exist. Wurtz attempted to prepare it by the action of bromide of ethylene on bisodic glycol, expecting the reaction to take place according to the equation:

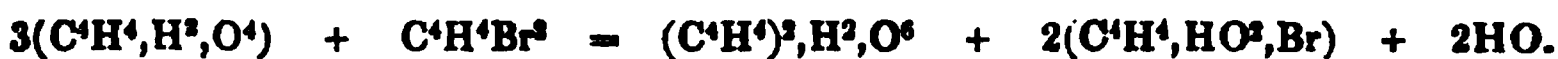


but the only products obtained were bromide of aldehydene,  $\text{C}^4\text{H}^3\text{Br}$  and glycol (p. 424); and again by the action of bromide of aldehydene on monosodic glycol, according to the equation:



but the products obtained were chiefly olefiant gas and glycol (p. 424). — Wurtz was at one time of opinion that the aldehydes were the true ethers of the glycols, because glycol treated with chloride of zinc (p. 428) yields aldehyde: but that compound does not reproduce glycol when treated with water, or compound glycolic ethers when treated with acids, as oxide of ethylene does.

*Intermediate Glycol-ether.*  $C^8H^{10}O^6 = (C^4H^4)^2, H^2, O^6$ . — Produced, together with glycolic bromhydrin, by heating 3 at. glycol with 1 at. bromide of ethylene (equal weights of the two) to  $120^\circ$  for four days in a sealed flask. (Lourenço.)



Also, together with glycol, by heating oxide of ethylene with water in a sealed tube. (Wurtz.)



Syrupy liquid, having a sweetish taste. Boils at about  $245^\circ$ . Vapour density 3.78 (at  $311^\circ$ ). Soluble in water, alcohol, and ether. (Lourenço, *Compt. rend.* 49, 619).

Lourenço.								Vol.	Density.			
8 C	.....	48	...	45.28	...	45.16	.....	C-vapour	...	8	...	3.3280
10 H	.....	10	...	9.43	...	9.56	.....	H-gas	...	10	...	0.6930
6 O	.....	6	...	45.29	...	45.28	.....	O-gas	...	3	...	3.3279
<hr/>												
C <sup>8</sup> H <sup>10</sup> O <sup>6</sup>	.....	64	...	100.00	...	100.00	.....	Vapour	...	2	...	7.3489
										1	...	3.6744

This body is intermediate in composition between glycol and oxide of ethylene, and might be regarded as a compound of the two:  $C^4H^6O^4 + C^4H^4O^2 = C^8H^{10}O^6$ . — Or it may be viewed as a product of the union of two molecules of glycol, with elimination of 2 at. water  $2(C^4H^4, H^2, O^4) - 2HO = (C^4H^4)^2, H^2, O^6$  (Lourenço).

*Ethyl-glycol or Ethylate of Ethylene.*  $C^8H^{10}O^4 = \left. \begin{matrix} C^4H^4 \\ C^4H^5, H \end{matrix} \right\} O^4$ . — Produced by the action of iodide of ethyl on monosodic glycol:

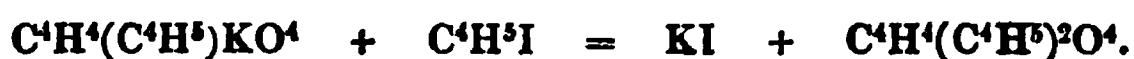


4.5 grammes of sodium were dissolved in 12 grammes of glycol, 27 grammes of iodide of ethyl added, and the whole heated to  $100^\circ$  in a flask surmounted with a bulb-tube for condensing the vapours. On distilling the product in an oil-bath heated gradually to  $250^\circ$ , a quantity of limpid ethereal liquid passed over, weighing 10 grms., and 29 grms. of iodide of sodium were left in the flask (calculated quantity, 26.9 grms.) The ethereal liquid began to boil at  $110^\circ$ , the thermometer then rose quickly to  $120^\circ$ , and the greater part of the liquid passed over between  $125^\circ$  and  $135^\circ$ : this latter product when redistilled passed over entirely at  $127^\circ$ . In another operation, when 6 grms. of glycol and 2 grms. of sodium were used, the product yielded by fractional distillation a liquid boiling at  $135^\circ$ . (Wurtz.)

						Wurtz.	
						At 135°.	At 127°.
8 C	.....	48	.....	53.33	.....	54.90	..... 57.35
10 H	.....	10	.....	11.11	.....	11.18	..... 11.59
4 O	.....	32	.....	35.56	.....		.....
<hr/>							
C <sup>8</sup> H <sup>10</sup> O <sup>4</sup>	.....	90	.....	100.00			

These numbers show that the liquids analysed were mixtures of ethyl-glycol and biethyl-glycol (61.01 C and 11.86 H), the ethyl-glycol predominating considerably in the product which boiled at 127°. The simultaneous formation of biethyl-glycol is unavoidable, because, in the action of sodium on glycol, the compound  $C^4H^4Na^2O^4$  is formed, as well as  $C^4H^6NaO^4$ . To obtain a complete separation of the two liquids, it would be necessary to operate on very large quantities. The boiling point of ethyl-glycol is intermediate between that of glycol (197°) and that of biethyl-glycol (123°). The vapour-density of the liquid boiling at 127° was found to be 3.418, intermediate between the calculated vapour-density of ethyl-glycol, 3.116, and that of biethyl-glycol, 4.085.

*Biethyl-glycol* or *Biethylate of Ethylene*.  $C^{12}H^{14}O^4 = C^4H^4(C^4H^5)^2O^4$ .—The ethereal liquid containing ethyl-glycol, yields when treated with potassium, the compound  $\left. \begin{matrix} C^4H^4 \\ C^4H^5, K \end{matrix} \right\} O^4$ ; and this compound is decomposed by iodide of ethyl, yielding biethyl-glycol:



2 grms. of potassium were added by small portions to 7.5 grms. of the ethereal liquid containing ethyl-glycol, and the resulting white solid mass was treated with 8 grms. of iodide of ethyl. An immediate reaction took place, and the product yielded by distillation 9 grms. of ethereal liquid, which was again treated with a globule of potassium and a few drops of iodide of ethyl, and finally rectified over potassium.

Colourless, very mobile liquid, having a very agreeable ethereal odour. Sp. gr. 0.7993 at 0°. Boils at 123.5° with the barometer at 758.8 mm. Vapour-density 4.095°.

Wurtz.										Vol.	Density.			
12 C	.....	72	....	61.02	....	61.06	....	61.18	.....	C-vapour	....	12	....	4.9920
14 H	.....	14	....	11.86	....	12.03	....	12.31	.....	H-gas	....	14	....	0.9702
4 O	.....	32	....	27.12	....	26.91	....	26.51	.....	O-gas	....	2	....	2.2186
<hr/>														
C <sup>12</sup> H <sup>14</sup> O <sup>4</sup>	....	118	....	100.00	....	100.00	....	100.00	Vap. of C <sup>12</sup> H <sup>14</sup> O <sup>4</sup>	....	2	....	8.1808	
											1	....	4.0904	

Isomeric with acetal, from which however it is distinguished by its higher boiling point, acetal boiling at about 104° (ix, 39).

*Glycolic Chlorhydrin*.  $C^4H^5ClO^3 = C^4H^4, HO^3, Cl$ . — *Glycol-monochlorhydrine*. (Wurtz). Obtained by saturating glycol with hydrochloric acid gas, heating the liquid to 100° in a sealed tube, and repeating these operations till the liquid, on being removed from the tube, no longer gives off fumes of hydrochloric acid:



On distilling a product thus obtained, water containing hydrochloric acid passed over at first, but the thermometer soon rose to 110°; a considerable portion of liquid passed over between 110° and 114°; and the whole, with the exception of undecomposed glycol, by the time the thermometer had risen to 140°. The liquid which distilled between 110° and 114° was still acid and contained water. After several fractional distillations, the boiling point of the liquids which had passed over above 114° rose to about 130°, and ultimately glycolic chlorhydrin was obtained in the form of a colourless, neutral liquid, boiling at 128°. Its solution dissolves in water in all proportions, and when placed in the flame of a lamp takes fire and colours the flame green.

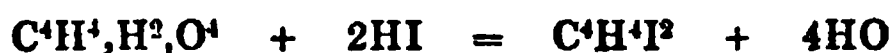
				Wurtz.
4 C	.....	24.0	.....	29.82
5 H	.....	5.0	.....	6.21
Cl	.....	35.5	.....	44.09
2 O	.....	16.0	.....	19.88
<hr/>				
C <sup>4</sup> H <sup>5</sup> ClO <sup>2</sup>	.....	80.5	.....	100.00

May be regarded as glycol C<sup>4</sup>H<sup>4</sup>,HO<sup>2</sup>,HO<sup>2</sup>, in which one molecule of HO<sup>2</sup> is replaced by Cl.

The *bichlorhydrin of glycol* is chloride of ethylene, C<sup>4</sup>H<sup>4</sup>Cl<sup>2</sup>.

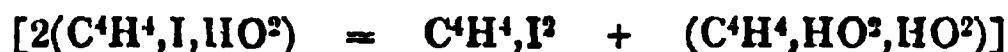
*Glycolic Bromhydrin*: C<sup>4</sup>H<sup>5</sup>BrO<sup>2</sup>.— Produced, together with the intermediate ether of glycol, by the action of bromide of ethylene on glycol (Lourenço, p. 426).

*Glycolic Iodhydrin*. C<sup>4</sup>H<sup>5</sup>IO<sup>2</sup>. — Hydriodic acid is rapidly absorbed by glycol, great heat being evolved, and the liquid becoming black and thick from separation of iodine; and on removing the iodine by dilute potash, a mass of white crystals is obtained, consisting of iodide of ethylene:



If however the temperature be prevented from rising by surrounding the vessel with cold water during the passage of the gas, a liquid product is obtained, which, after being treated with metallic silver to remove free iodine, exhibits approximately the composition of glycolic iodhydrin, viz., 11.1 p. c. carbon and 3.5 hydrogen, the formula C<sup>4</sup>H<sup>5</sup>IO<sup>2</sup> requiring 13.9 C and 3.0 H.

Glycolic iodhydrin is soluble in water and alcohol, but insoluble in ether. It has no taste at first, but almost burns the tongue after a time. It is decomposed by heat into iodide of ethylene, and probably glycol:



It acts with great energy on silver-salts. — Potash decomposes it, yielding iodide of potassium and oxide of ethylene (Simpson):



*Sulphoglycolic acid*. C<sup>4</sup>H<sup>6</sup>S<sup>2</sup>O<sup>10</sup> = C<sup>4</sup>H<sup>6</sup>O<sup>4</sup>,S<sup>2</sup>O<sup>6</sup>. — Produced by heating a mixture of glycol and monohydrated sulphuric acid to 150°:



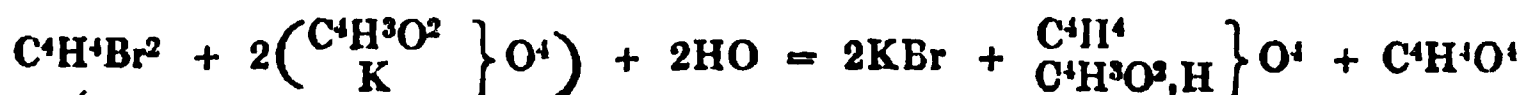
It is not known in the free state. The barium-salt is obtained by diluting the above-mentioned mixture with water, filtering, and evaporating to a syrup over the water-bath, whereupon it separates as white solid mass, which may be purified by pressure between paper and evaporation in vacuo over oil of vitriol. It is somewhat deliquescent and does not readily crystallise. Decomposes slightly at 100°. Easily soluble in water, nearly insoluble in absolute alcohol and in ether. From the aqueous solution, sulphuric acid throws down sulphate of baryta. Baryta-water occasions no precipitate in the cold; but on heating the liquid for some time, it becomes turbid, from separation of the same salt. (Simpson, *Proc. Roy. Soc.* 9, 725.)



<i>Dried in vacuo over Oil of Vitriol.</i>					Simpson.
4 C	.....	24.0	....	11.45	..... 10.71
5 H	.....	5.0	....	2.40	..... 2.79
BaO	.....	76.5	....	36.15	..... 36.50
2 SO <sup>3</sup>	.....	80.0	....	38.51	..... 38.09
3 O	.....	24.0	....	11.49*	..... 11.91
<hr/> C <sup>4</sup> H <sup>3</sup> BaS <sup>2</sup> O <sup>10</sup>					..... 209.5 .... 100.00 ..... 100.00

The salt is analogous to Pelouze's sulphoglycerate of baryta (ix, 494). Simpson represents its composition by the formula C<sup>4</sup>H<sup>3</sup>O<sup>2</sup>,S<sup>2</sup>O<sup>4</sup>,Ba,O<sup>1</sup>.

*Monoacetate of Ethylene.* C<sup>3</sup>H<sup>3</sup>O<sup>6</sup> =  $\left. \begin{matrix} \text{C}^4\text{H}^4 \\ \text{C}^4\text{H}^3\text{O}^2, \text{H} \end{matrix} \right\} \text{O}^4$ . — *Monoacetate of Glycol. Glycolic monoacetin.* — Obtained: 1. By the action of acetate of potash on bromide of ethylene (Atkinson):



1 pt. of pure bromide of ethylene and 1 pt. of acetate of potash, together with 2 pts. of 85 per cent. alcohol, are heated for two days to 100° in a strong flask (a soda-water bottle answers very well) securely corked. Bromide of potassium is then formed, together with a colourless liquid containing monoacetate of ethylene, acetic acid, and acetic ether (formed by the action of the acetic acid on the alcohol) besides alcohol and water. On distilling it, monoacetate of glycol mixed with acetic acid passes over between 130° and 180°, and nearly pure monoacetate from 180° to 185°. By repeated rectification of these liquids, the pure monoacetate is obtained, boiling at 182°. — In the first distillation the liquid often jumps violently in consequence of the separation of a little bromide of potassium; in this case, an equal volume of ether must be added to precipitate the bromide of potassium, and the liquid filtered (Atkinson). Simpson recommends, especially for the preparation of large quantities of the monoacetate, to heat the materials, not in a closed vessel but in a large flask connected with a Liebig's condenser in such a manner as to cause the condensed vapour to flow back into the vessel. — 2. By the action of acetate of potash on *chloride of ethylene*. The decomposition does not take place so readily as with the bromide, and requires the mixture to be heated for three or four days (Atkinson). — 3. By heating a mixture of 1 at. glycol and 1 at. acetic anhydride in a sealed tube for several hours at a temperature not exceeding 170°, and collecting apart the liquid which, in the subsequent distillation, passes over between 180° and 186° (Simpson).



Monoacetate of ethylene is a colourless, oily liquid, boiling at 182°. It is heavier than water, and miscible with water and with alcohol. The aqueous solution is neutral.

					• Atkinson.	Simpson.
8 C	.....	48	....	46.0	..... 45.1	..... 46.02
8 H	.....	8	....	7.7	..... 7.8	..... 7.80
6 O	.....	48	....	46.3	..... 47.1	..... 46.18
<hr/>						
C <sup>8</sup> H <sup>8</sup> O <sup>6</sup>	.....	104	....	100.0	..... 100.0	..... 100.00

May be regarded as C<sup>4</sup>H<sup>4</sup>,C<sup>4</sup>H<sup>3</sup>O<sup>4</sup>,HO<sup>2</sup>, that is to say as glycol in which 1 At. HO<sup>2</sup> is replaced by peroxide of acetyl C<sup>4</sup>H<sup>3</sup>O<sup>4</sup>.



This compound is easily decomposed by potash or baryta, yielding glycol and an acetate of the base. — On heating 2.027 grms. of it with hydrate of baryta and water in a sealed tube to between 120° and 130° for 25 hours, removing the excess of baryta from the filtrate by carbonic acid, evaporating to dryness, treating the residue with water, and decomposing the filtered solution with sulphuric acid, a precipitate of sulphate of baryta was obtained, weighing 2.126 grms. corresponding to 2.38 grms. of acetate of baryta,  $C^4H^3BaO^4$ , or 1.1 gm. of acetic acid  $C^4H^4O^4$ . — According to the formula  $C^4H^4, C^4H^3O^2, HO^4$ , the quantity of acetate of baryta obtained should have been 2.485 grms. (Atkinson.)

*Biacetate of Ethylene.*  $C^{12}H^{10}O^8 = \left. \begin{matrix} C^4H^4 \\ (C^4H^3O^2)^2 \end{matrix} \right\} O^4$ . Preparation (xii. 503). — Bromide of ethylene may be advantageously substituted for the iodide. Sp. gr. 1.128 at 0°. Boiling point between 186° and 187°. — Vapour density 4.744 (Wurtz).

						Wurtz.			Vol.	Density.
12 C .....	96	...	49.31	...	48.59	...	C-vapour .....	12	...	4.9920
10 H .....	10	...	6.84	...	7.30	...	H-gas .....	10	...	0.6930
8 O .....	64	...	43.85	...	44.11	...	O-gas .....	4	...	4.4372
<hr/>										
C <sup>12</sup> H <sup>10</sup> O <sup>8</sup> .....	170	...	100.00	...	100.00	...	Vap. of C <sup>12</sup> H <sup>10</sup> O <sup>8</sup>	2	...	10.1222
								1	...	5.0611

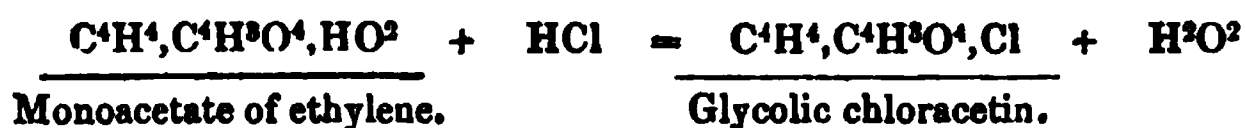
When poured into a small quantity of water, it sinks to the bottom in the form of an oil. It dissolves in 7 pts. of water at 22°, and is separated from the solution by chloride of calcium. Alcohol and ether dissolve it in all proportions (Wurtz).

*Basic Acetate of Ethylene.*  $C^{16}H^{14}O^{10} = (C^4H^4)^2(C^4H^3O^2)^2O^6$  — Formed, together with the biacetate, by treating oxide of ethylene at ordinary temperatures, with glacial acetic acid or acetic anhydride. On distilling the product, biacetate of ethylene passes over at about 185°, and the basic acetate at a much higher temperature. This product has not yet been analysed: if the above formula be correct, it may be regarded as 2 at. oxide of ethylene + 1 at. acetic anhydride:  $2C^4H^4O^2 + C^6H^6O^6$  (Wurtz, *Bull. Soc. Chim. de Paris.* i, 79).

In the paper just referred to, Wurtz expresses an opinion that this compound may be identical with a liquid which is obtained as an accessory product in the preparation of biacetate of ethylene by the action of iodide of ethylene on acetate of silver. This liquid distills at 260° and yields by analysis 46.1 and 46.5 p. c. carbon. and 5.9 and 6.2 p. c. hydrogen, whence Wurtz (*N. Ann. Chim. Phys.* 55, 405) originally deduced the formula  $C^{16}H^{12}O^{12}$  or  $\left. \begin{matrix} C^4H^3 \\ (C^4H^3O^2)^3 \end{matrix} \right\} O^6$ , representing the compound as a teracetin containing the radical  $C^4H^3$ , homologous with and next below  $C^6H^5$ , the radical of the glycerine-compounds. This formula requires 47.0 p. c. C and 5.9 H, numbers approaching much more nearly to the results of analysis than those required by the formula of basic acetate of ethylene,  $C^{16}H^{14}O^{10}$ , viz., 50.5 p. c. C and 7.37 H. On the other hand, the formation of glycerine-compound from iodide of ethylene does not appear very probable. The compound requires further investigation.

*Glycolic Chloracetin.*  $C^8H^7ClO^4 = C^4H^4, C^4H^3O^4, Cl$ . — Obtained by passing dry hydrochloric acid gas into monoacetate of ethylene (which need not be perfectly pure) at the temperature of 100°, till the quantity of oily liquid separated on the addition of water ceases to increase. The whole is then treated with water, and the precipitated oil is well washed with water, dried over chloride of calcium, and distilled, nearly the whole

passing over between  $114^{\circ}$  and  $116^{\circ}$  (Simpson, *Proc. Roy. Soc.* 10, 115). The mode of formation is as follows :



Simpson first prepared this compound (*Proc. Roy. Soc.* 9, 726) by saturating with hydrochloric acid a mixture of glycol and acetic acid in equivalent proportions, heating this mixture to  $100^{\circ}$  in a sealed tube to  $400^{\circ}$ , and separating the chloracetin with water as above; but the use of the monoacetate is much to be preferred. — 2. By the action of chloride of acetyl on glycol (Lourenço).

Colourless liquid, having a specific gravity of 1.1783 at  $0^{\circ}$ . Boils at  $145^{\circ}$ , distilling without decomposition. Vapour-density, 4.369.

Simpson.						Vol. Density.	
8 C	48.0	39.18	39.01	38.97	C-vapour	8	3.3280
7 H	7.0	5.71	5.83	6.07	H-gas	7	0.4851
Cl	35.5	28.97		27.48	Cl-gas	1	2.4543
4 O	32.0	26.14			O-gas	2	2.2186
<hr/>							
$\text{C}^8\text{H}^7\text{ClO}^4$	122.5	100.00			Vapour	2	8.4860
						1	4.2430

May be regarded as glycol  $\text{C}^4\text{H}^4, \text{HO}^2, \text{HO}^2$ , in which 1 At.  $\text{HO}^2$  is replaced by peroxide of acetyl,  $\text{C}^4\text{H}^3\text{O}^4$ , and the other by chlorine. It is isomeric with the compound which Simpson obtained by the action of chloride of acetyl on aldehyde (p. 440), from which however it is distinguished by its higher boiling point and by its behaviour with potash; also with the compound which Wurtz obtained by the action of chlorine on aldehyde (xii, 536).

Glycolic chloracetin is scarcely, if at all decomposed by cold water, and with difficulty by boiling water. Heated with potash, it yields oxide of ethylene, together with chloride and acetate of potassium:



*Glycolic Iodacetin.*  $\text{C}^8\text{H}^7\text{IO}^4 = \text{C}^4\text{H}^4, \text{C}^4\text{H}^3\text{O}^4, \text{I}$ . — Obtained by passing hydriodic acid gas into monacetate of ethylene, or a mixture of equivalent quantities of glacial acetic acid and glycol, internally cooled, till a portion of the liquid gives a considerable oily precipitate on the addition of water: if the passage of the gas be further continued, iodide of ethylene is likely to be formed. — The product is well washed with very dilute potash and dried in vacuo.

Glycolic iodacetin is, at ordinary temperatures, an oily liquid, having a sweetish pungent taste; at low temperatures it crystallises in tables. It sinks in water, and is insoluble in that liquid, but dissolves in alcohol and ether. Heated with potash, it yields iodide of potassium; acetate of potash, and oxide of ethylene (Simpson).

Simpson.					
		<i>a.</i>		<i>b.</i>	<i>c.</i>
8 C	48	22.42	21.95	22.30	22.62
7 H	7	3.27	3.31	3.50	3.43
I	127	14.96			
4 O	32	59.35			
<hr/>					
$\text{C}^8\text{H}^7\text{IO}^4$	214	100.00			

*a* and *b* were prepared from a mixture of glycol and acetic acid; *c* from monacetate of ethylene. (Simpson.)

*Oxalate of Ethylene.*  $C^2(H^4)O^8$ . — Appears to be formed by the action of bromide of ethylene on oxalate of silver. 100 grms. of this salt were triturated with 60 grms of bromide of ethylene, and the mixture was heated to  $100^\circ$  for several days. The residue was then exhausted with ether, the ethereal solution treated with lime, and the liquid filtered and distilled in the water-bath. A small quantity of liquid remained, having a saccharine taste, insoluble in water, boiling at a high temperature, but appearing to decompose by distillation. Treated with ammonia it gave immediately a precipitate of oxamide (Wurtz, *N. Ann. Chim. Phys.* 55, 438).

*Bibutyrate of Ethylene.* —  $C^{20}H^{18}O^8 = C^4H^4(C^8H^7O^2)^2O^4$ . *Bibutyrate of Glycol, Glycol dibutyrique.* — Obtained by heating for several hours on the water-bath, a paste composed of 90 grms. (2 At.) butyrate of silver, 48 grms. (1 At.) of bromide of ethylene, and a sufficient quantity of butyric acid, exhausting the product with ether, and distilling. After the ether has passed over, the greater part of the remaining liquid distils between  $230^\circ$  and  $240^\circ$ , and by fractional distillation, butyrate of ethylene is obtained boiling between  $239^\circ$  and  $241^\circ$ .

Colourless liquid, having a strong butyric odour, which is rather persistent when the liquid is rubbed on the skin. Sp. gr. 1.024 at  $0^\circ$ . Boils at about  $240^\circ$  and distils without alteration. Perfectly insoluble in water, but dissolves in all proportions in alcohol or ether.

						Wurtz.
20 C	.....	120	....	59.40	.....	59.63
18 H	.....	18	....	8.91	.....	9.18
4 O	.....	32	....	31.69	.....	31.79
<hr/>						
$C^{20}H^{18}O^4$	.....	170	....	100.00	.....	100.00

0.535 gram. of the above product, boiling at  $240^\circ$ , heated in a sealed tube with a standard solution of baryta-water, neutralised a quantity of baryta equivalent to 0.246 of monohydrated sulphuric acid, corresponding to 0.442 butyric acid. Hence 1 At. butyric glycol contains 1.89 At., that is to say, 2 At. butyric acid. — 0.310 gram. of the product, boiling at  $230^\circ$ , similarly treated, neutralised a quantity of baryta corresponding to 0.150 gram. of monohydrated sulphuric acid, and therefore equivalent to 0.269 butyric acid, which gives 1.99 or 2 At. butyric acid for 1 At. of the compound analysed (Wurtz).

*Glycolic Chlorobutyrim.*  $C^{12}H^{11}ClO^4 = C^4H^4, C^8H^7O^4, Cl$ . — Prepared, similarly to glycolic chloracetin, by passing dry hydrochloric acid gas through a mixture of equivalent quantities of butyric acid and glycol, heated to  $100^\circ$ ;



The product must be well washed with water, dried over chloride of calcium and distilled. The greater part goes over between  $160^\circ$  and  $182^\circ$ , and on rectifying this distillate, the portion which distils between  $175^\circ$  and  $182^\circ$ , yields the chlorobutyrim. (Simpson, *Proc. Roy. Soc.* 10, 117).

Colourless liquid, having a pungent, somewhat bitter taste, sp. gr. 1.0854 at  $0^\circ$ . Boils at about  $190^\circ$ . Insoluble in water, but freely soluble in alcohol.

					Simpson.
12 C	.....	72.0	...	47.84	..... 47.76
11 H	.....	11.0	...	7.30	..... 7.81
Cl	.....	35.5	...	23.58	..... 23.88
4 O	.....	32.0	...	21.28	..... 21.05
<hr/>					
$C^{12}H^{11}ClO^4$	.....	150.5	...	100.00	..... 100.00

Glycolic chlorobutyrim is decomposed with difficulty by a boiling solution of potash, but readily by solid potash, yielding chloride of potassium, butyrate of potash, and oxide of ethylene. With acetate of silver it yields acetobutyrate of ethylene. (Simpson.)

*Acetobutyrate of Ethylene.* —  $C^{16}H^{14}O^8 = C^4H^4, C^4H^3O^4, C^8H^7O^4$ . — *Butyroacetate of Glycol, Glycolic Acetobutyrim or Butyroacetin.* — Prepared by heating equivalent quantities of glycolic chloracetin and butyrate of silver in a long-necked flask to between  $100^\circ$  and  $200^\circ$ , till all the silver-salt is converted into chloride :



The product is digested with ether, filtered and distilled. As soon as the ether has passed off, the thermometer rises quickly to  $180^\circ$ , and between  $180^\circ$  and  $215^\circ$  almost the whole passes over; and this portion, submitted to fractional distillation, yields acetobutyrate of ethylene between  $208^\circ$  and  $215^\circ$ . — 2. By heating in like manner a mixture of glycolic chlorobutyrim and acetate of silver, care being taken however that the temperature does not rise above  $150^\circ$ . (Simpson.)

Colourless liquid, heavier than water, insoluble in water, but soluble in alcohol. It has a bitter pungent taste. It is very stable, solution of potash decomposing it but slowly, even at the boiling heat.

					Simpson.					
					a.		b.		c.	
18 C	.....	108	....	55.17	.....	54.31	...	55.58	...	56.29
14 H	.....	14	....	8.04	.....	8.20	...	7.97	...	8.75
8 O	.....	64	....	36.79	.....					
<hr/>										
C <sup>18</sup> H <sup>14</sup> O <sup>8</sup>	.....	186	....	100.00						

*a* and *b* were prepared by the first method, *c* by the second; the latter could not be purified on account of the smallness of the quantity available. (Simpson).

*Bibenzoate of Ethylene.*  $C^{28}H^{14}O^8 = C^4H^4(C^{14}H^5O^2)^2, O^4$ . — *Glycol dibenzoique.* 68 grms. of benzoate of silver (rather more than 2 At.) and 29 grms. (1 At.) bromide of ethylene are heated for several days to  $100^\circ$  in a long-necked flask; the product is taken up with ether, and the solution is treated with a small quantity of slaked lime, then filtered and distilled in the water-bath. The residue on cooling becomes filled with crystals, which are to be separated from the mother-liquor, pressed between paper, and purified by several recrystallizations from ether.

By spontaneous evaporation of the ethereal solution, the compound is deposited in shining, colourless, right rhomboidal prisms, which melt at  $67^\circ$ , forming a liquid which boils at a temperature above the boiling point of mercury, and distils without alteration (Wurtz, *N. Ann. Chim. Phys.* 55, 437).

					Wurtz.
32 C	.....	192	...	71.11	..... 71.16
14 H	.....	14	...	5.18	..... 5.35
8 O	.....	64	...	23.71	..... 23.49
<hr/>					
$C^{32}H^{14}O^8$	.....	270	...	100.00	..... 100.00

Benzoate of ethylene is decomposed when heated, even with dilute potash, yielding glycol and benzoate of potash. 0.713 grm. saponified with pure potash, then neutralized with nitric acid and precipitated by nitrate of silver, yielded 1.142 grm. of benzoate of silver. Hence it may be inferred that 1 At. of the compound contains 1.9, that is to say 2 At. of benzoic acid. (Wurtz.)

*Bistearate of Ethylene.*  $C^{76}H^{74}O^8 = C^4H^4(C^{36}H^{36}O^3)^2O^4$ . — Obtained by decomposing stearate of silver with bromide of ethylene, and treating the product with ether, &c., as in the preparation of the preceding compound. Small light, shining scales, melting at  $76^\circ$ , and having very much the aspect of stearin. (Wurtz.)

					Wurtz.
76 C	.....	456	...	76.76	..... 76.25
74 H	.....	74	...	12.46	..... 12.69
8 O	.....	64	...	10.78	..... 11.16
<hr/>					
$C^{76}H^{74}O^8$	.....	594	...	100.00	..... 100.00

### Glyoxylic Acid. $C^4H^2O^6$ .

DEBUS. *Ann. Pharm.* 110, 316; abstr. *Proc. Roy. Soc.* 9, 711.

Formation by oxidation of glycol (p. 423). — It is also formed, as an intermediate product in the oxidation of glyoxal  $C^4H^2O^4$ , by nitric acid, the ultimate product of the reaction being oxalic acid  $C^4H^2O^8$ .

*Glyoxylate of Ammonia.*  $C^4H(NH^4)O^6$ . — Prepared by precipitating glyoxylate of lime with its equivalent quantity of oxalate of ammonia and evaporating the filtrate over oil of vitriol in vacuo. It is then obtained in small colourless prismatic crystals which dissolve readily in water. The concentrated solution turns yellow when boiled or when evaporated at  $100^\circ$ . With nitrate of silver and acetate of lead, it forms crystalline precipitates at once, but with sulphate of copper, after some time only. Potash evolves ammonia from it, even at common temperatures.

<i>Dried in vacuo over oil of vitriol.</i>					Debus.
4 C	.....	24	...	26.37	..... 26.96
5 H	.....	5	...	5.49	..... 5.70
N	.....	14	...	15.40	.....
6 O	.....	48	...	52.74	.....
<hr/>					
$C^4H(NH^4)O^6$	...	91	...	100.00	

The composition of this salt shows that the formula of glyoxylic acid is  $C^4H^2O^6$ , not  $C^4H^4O^6$  (xii, 506). Nevertheless, most of the glyoxylates contain 2 At. water, of which they cannot be deprived without decomposition.

*Glyoxylate of Baryta.*  $C^4HBaO^6 + 4HO$ . — Prepared by digesting diluted glyoxylic acid at ordinary temperatures with carbonate of baryta till the acid is completely neutralized, and evaporating the filtrate in vacuo. At a certain degree of concentration, the salt begins to separate in small white crystals. It is partly resolved into glycolic acid and oxalate of baryta, when heated to  $120^\circ$ , or when its aqueous solution is raised to the boiling point. With lime-water, acetate of lead, and nitrate of silver, it behaves like the lime-salt. — By analysis it gives 39.4 p.c. barium, the above formula requiring 38.9 p.c.

*Glyoxylate of Lime.*  $C^4HCaO^6 + 4HO$ . (xii, 507). — Lime-water added to the solution of this salt immediately produces a copious precipitate, which, immediately after its formation, dissolves readily in acetic acid, but if left to itself for a while, or more quickly if boiled for a few seconds with the liquid, becomes insoluble in acetic acid, being in fact resolved into glycolate and oxalate of lime :



This reaction affords the means of separating glyoxylic from glycolic acid, when the two occur together, a solution of pure glycolate of lime not being precipitated by lime-water. It also serves for the quantitative estimation of glyoxylic acid, 128 pts. (1 At.) of oxalate of lime ( $C^4H^2O^8$ ) corresponding to 222 pts. (1 At.) of the glyoxylate ( $C^4HCaO^6 + 4HO$ ).

*Glyoxylate of Zinc.*  $C^4HZnO^6 + 4HO$ . — Produced as a white crystalline precipitate by adding a strong solution of glyoxylate of lime to acetate of zinc. It dissolves, sparingly in water, easily in acetic acid, hydrochloric acid, and caustic potash. After drying over oil of vitriol, it gave by analysis 38.09 and 38.73 p.c. zinc, the formula requiring 37.64 per cent. The 4 At. water cannot be removed without decomposing the salt.

*Glyoxylate of Silver.*  $C^4HAgO^6 + 2HO$  is obtained as a white crystalline powder by precipitating nitrate of silver with glyoxylate of ammonia. It is but sparingly soluble in cold water, and is rapidly decomposed by light. Analysis gave 54.1 and 53.9 p.c. silver, the formula requiring 54.2 per cent. (Debus.)

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### Glycolic Acid. $C^4H^4O^6$ .

KEKULÉ. *Ann. Pharm.* 105, 286.

*Formation from Chloracetic Acid.* — The suggestion of R. Hofmann (xii, 539) that glycolic acid is formed, together with a metallic chloride, when a hydrated salt of chloracetic acid is decomposed by heat, according to the equation,



has been confirmed by Kekulé. Chloracetate of potash, heated for some

time to  $110^{\circ}$ – $120^{\circ}$ , becomes moist, and acquires a yellowish colour and acid reaction. On treating the mass with water, chloride of potassium and glycolic acid dissolve, and a small quantity of a white powder, sparingly soluble in hot water, remains behind. This white substance is probably *glycolide* ( $C^4H^2O^4$ ), inasmuch as it is converted into glycolic acid by boiling with water, and into glycolate of lime by boiling with lime water. Its formation is represented by the equation :



That the quantity of it produced is small in comparison with that of the glycolic acid, arises from the presence of water in the chloracetate of potash, which water cannot be separated, without at the same time inducing the decomposition of the salt in the manner represented by the first equation.

To obtain the glycolic acid, the dried mass is treated with a mixture of alcohol and ether, whereby a solution is obtained, which when evaporated, leaves the acid in the form of a yellowish syrup. Or glycolate of lime may be prepared from the solution of the acid containing chloride of potassium, by boiling it with lime-water, removing the excess of lime with carbonic acid, and leaving the somewhat concentrated solution to cool. The glycolic acid may also be obtained at once, very pure and perfectly colourless, by boiling the aqueous solution of monochloracetate of potash for a considerable time, or better by heating it for some hours to  $120^{\circ}$ – $140^{\circ}$  in a closed tube, and then separating the acid from the chloride of potassium as above.

The acid thus prepared does not crystallize, but if it be separated from the silver-salt by sulphuretted hydrogen, and the liquid evaporated, the syrupy mass quickly separates in large, very deliquescent crystals grouped in stars.

Chloracetate of ammonia decomposes when heated, exactly like the potash-salt, yielding glycolic acid and sal-ammoniac ;



The salts obtained from the acid thus prepared agree perfectly with those previously described.

*Glycolate of lime*, obtained by boiling the dry acid with lime-water, removing the excess of lime by carbonic acid, and concentrating the filtrate, separates on cooling, in stellate groups of extremely fine asbestos-like needles, which contain so much mother-liquor enclosed, that the solution solidifies into a kind of pulp. The salt dissolves sparingly in cold water, but sufficiently to give a precipitate with alcohol. The needles contain water of crystallization, which they give off at  $100^{\circ}$ . The dried residue swells up strongly when heated, and burns away, leaving carbonate of lime.

	At $100^{\circ}$ .			Kekulé.	
4 C .....	24	...	25.26	.....	25.27
3 H .....	3	...	3.16	.....	3.28
Ca .....	20	...	21.05	.....	21.01
6 O .....	48	...	50.53	.....	50.44
<hr/>					
$C^4H^2CaO^4$ ....	95	...	100.00	.....	100.00



The glycolate of lime which Debus obtained, together with glyoxylate, by oxidizing glycol with nitric acid, &c. (p. 422), contained 5 At. water of crystallization; that which he had previously obtained (xii, 509) by neutralizing glycolic acid with chalk and precipitating with alcohol, contained, after drying over oil of vitriol, only 3 At. water. The 5-atom salt appears to give up part of its water, when kept for some time over oil of vitriol, the crystals losing their lustre. (Debus.)

*Glycolate of baryta*, prepared like the lime-salt, forms large transparent colourless crystals when the solution is not too much concentrated; if it be evaporated to a syrup, the salt separates in crystalline crusts.

*Glycolate of Lead*. — A hot aqueous solution of the lime-salt mixed with acetate of lead, yields on cooling small needles grouped in nodules.

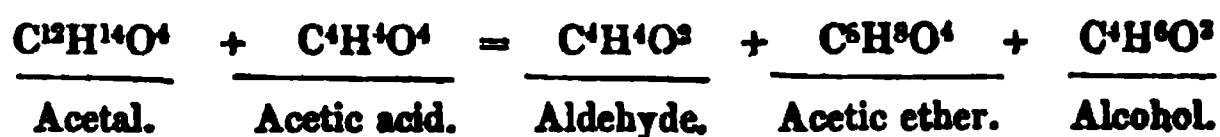
*Glycolate of Silver*. — On mixing a hot aqueous solution of glycolate of lime with nitrate of silver, glycolate of silver separates on cooling in crystalline spangles if the solution is rather strong; from a more dilute solution it is deposited in laminæ, more than a line in length. It is sparingly soluble in cold water; hot water dissolves it, with decomposition and reduction of silver. It is insoluble in alcohol, and is precipitated by alcohol in spangles from its aqueous solution.

	At 100°			Kekulé.	
4 C .....	24	...	13.11	.....	13.12
3 H .....	3	...	1.64	.....	1.65
Ag .....	108	...	59.02	.....	59.03
6 O .....	48	...	26.23	.....	26.20
<hr/>					
C <sup>4</sup> H <sup>3</sup> AgO <sup>6</sup> .....	183	...	100.00	.....	100.00

Page 274.

## Aldehyde.

*Formation from Acetal*. — When acetal is heated for two days with *glacial acetic acid* to a temperature between 150° and 200°, aldehyde is formed, together with acetic ether and alcohol, the aldehyde passing over below 60° when the product is distilled;



Acetal distilled with *acetic anhydride*, yields aldehyde and acetic ether:



A few drops of a liquid are also obtained, which boils above 150°, and is probably the compound of aldehyde and acetic anhydride discovered by Geuther (Beilstein, *Compt. rend.* 48, 1121).



**Formation from Sulphovinic Acid.** — When sulphovinic acid is heated with peroxide of manganese or chromate of potash, aldehyde is formed, even under circumstances which preclude the supposition of a previous formation of alcohol. — Dry sulphovinates, treated with the same oxidizing agents, also yield aldehyde, but mixed with oil of wine and other products of decomposition.

Amylsulphuric acid under the same circumstances yields valeral. (Jacquemin and Lies-Bodard, *Institut* 1857, 407.)

Aldehyde does not appear to be formed by the action of oxide of silver on chloride of ethylene. These substances do not act upon each other at the boiling heat; but when 1 At.  $C^4H^4Cl^2$  is heated with 2 At. AgO in sealed tubes to  $120^\circ$ , the oxide of silver is partially converted into chloride, and a liquid, boiling at a very low temperature, is formed, probably  $C^4H^2Cl$ , but no aldehyde. The same compound appears to be formed when chloride of ethylene is heated with excess of hydrate of potash in sealed tubes to  $125^\circ$  (Geuther, *Ann. Pharm.* 106, 321).

**Preparation of Aldehyde.** — The unproductiveness of the usual mode of preparing aldehyde by the action of chromic acid on alcohol, arises chiefly from the fact that a large quantity of the product is lost in the subsequent rectifications over chloride of calcium, partly on account of its great volatility, partly because it becomes oxidized into acetic acid by contact with the air. — To avoid these inconveniences, Städeler (*J. pr. Chem.*, 76, 54) connects the retort in which the materials are mixed, with a two-necked receiver, above which is placed an arrangement called a *dephlegmator*, consisting of an inverted bell-jar containing a worm-tube, the lower extremity of which is connected with the upper neck of the receiver, while the upper extremity is connected by a bent tube with a tall cylindrical glass vessel, which is itself connected with a second vessel of the same size and shape, and two-thirds filled with anhydrous ether. Both these vessels are surrounded with a mixture of ice and salt, and the *dephlegmator* is filled with water between  $50^\circ$  and  $60^\circ$ .

The materials used are 100 pta. of alcohol, 150 bichromate of potash in lumps as large as peas, and 200 sulphuric acid diluted with three times its bulk of water. The acid and water are first mixed in a separate vessel, and when the mixture is cold, the alcohol is added to it. The bichromate of potash is then introduced into the retort, which is surrounded with ice and salt, and the mixture of alcohol, water, and sulphuric acid, previously cooled in like manner, is added to it by small portions at a time, care being taken not to add the liquid fast enough to cause the contents of the retort to boil. The retort should be of such a size that the mixture fills it to about one-third, and must be provided with a funnel tube passing through the tubulus nearly to the bottom.

As soon as all the material is introduced into the retort, the freezing mixture is gradually removed, whereupon the contents begin to boil spontaneously; when this ceases, a very gentle heat must be applied, and gradually increased till, on taking out the funnel tube, the smell of aldehyde is no longer perceptible.

The next step of the process is to apply a gentle heat to the receiver by means of a small spirit-lamp, so as to drive the contents through the worm of the *diphlegmator*, which, as already observed, is heated to between  $50^\circ$  and  $60^\circ$ . Water, alcohol, acetal, and acetic ether, then condense in the worm and flow back into the receiver, while the aldehyde passes on and condenses, partly in the first cylindrical vessel, partly in the second, which contains ether.

When the distillation is ended, the contents of the two cylinders are mixed and saturated in a well cooled vessel with dry ammonia gas, introduced through a very wide conducting tube; the liquid is then left for twelve hours, and the separated crystals of aldehyde-ammonia are removed. The ethereal mother-liquor yields after some time an additional quantity of that compound in very large well developed crystals. 100 pts. of alcohol yield by this process about 40 pts. of aldehyde-ammonia.

To separate the aldehyde, the ammonia-compound is decomposed by dilute sulphuric acid, in a flask connected with a second flask containing chloride of calcium, and thoroughly cooled, the conducting tube passing down into it deep enough to come into contact with the chloride of calcium. This second flask is also connected with the worm of the diphlegmator, which is now to be used as a condensing apparatus, and filled with ice and water. As soon as all the aldehyde is distilled over into the second flask, the connecting tube between the two flasks is sealed in the middle, and a gentle heat is applied to drive the aldehyde through the diphlegmator, whence it passes into a cooled receiver.

*Decompositions of Aldehyde.* — 1. Dry hydrochloric acid gas passed to saturation into aldehyde, kept cool by a freezing mixture, converts it into *oxychloride of ethylidene*,  $C^2H^2Cl^2O^2$  (Lieben, p.453), which may be regarded as a double molecule of aldehyde, in which 2 At. O are replaced by 2 At. Cl.



Geuther & Cartmell (*Proc. Roy. Soc.* 10, 110), have also obtained, by the action of hydrochloric acid on aldehyde, the compound  $C^{12}H^{12}Cl^2O^4$ , in which 2 At. O in a triple molecule of aldehyde ( $C^4H^4O^6$ ) are replaced by 2 At. Cl.

2. With *pentachloride of phosphorus*, aldehyde forms *chloride of ethylidene*, an oily liquid, isomeric with Dutch liquid, but distinguished therefrom by its lower boiling point and specific gravity; and by not being decomposed by alcoholic potash in the cold, and but slowly when heated.

3. Pentabromide of phosphorus, in like manner converts aldehyde into *bromide of ethylidene*  $C^4H^4Br^2$ ; and this compound treated with *ethylate of soda*, yields acetal,  $C^{12}H^{14}O^4$ :



4. Aldehyde mixed with twice its volume of *anhydrous alcohol*, and saturated in the cold with dry hydrochloric acid gas, yields the compound  $C^6H^6ClO^2$  (p. 454);



and this compound treated with ethylate of sodium yields acetal:



This is an easier method of converting aldehyde into acetal, than the former. (Wurtz & Frapolli, *Ann. Pharm.* 108, 228.)

5. *Chlorocarbonic oxide* (phosgene) converts aldehyde into *chloracetene*,  $C^4H^3Cl$ , with evolution of hydrochloric and carbonic acids :



This reaction seems to shew that the rational formula of aldehyde is  $\left. \begin{matrix} C^4H^3 \\ H \end{matrix} \right\} O^2$ , rather than  $C^4H^3O^2, H$ . (Harnitz-Harnitzky, *Ann. Pharm.* 111, 192.)

*Compound of Aldehyde with Acetic Anhydride.*  $C^{12}H^{10}O^8 = C^4H^4O^2, C^8H^6O^6$ . — When equivalent weights of aldehyde and acetic anhydride are heated in a sealed tube to  $180^\circ$ , for twelve hours, and the product is distilled, free aldehyde and acetic anhydride pass over first, and afterwards, chiefly between  $160^\circ$  and  $170^\circ$ , a liquid, which, after being washed with hot water and dried over chloride of calcium, boils constantly at  $168.8^\circ$ . This is the compound in question. It has an alliaceous odour, and an acid reaction, arising probably from slight decomposition during distillation. Heated with hydrate of potash, it turns brown, gives out the same peculiar odour as aldehyde itself when similarly treated, and yields acetate of potash. It is not decomposed by anhydrous baryta, but if water is present, the same action takes place as with potash. Heated with nitrate of silver and excess of ammonia, it throws down grey metallic silver. (A. Geuther, *Ann Pharm.* 106, 249.)

					Geuther.				
					a.		b.		c.
12 C .....	72	...	49.32	.....	48.99	...	50.81	....	49.82
10 H .....	10	...	6.85	.....	6.96	...	6.74	....	6.96
8 O .....	64	...	43.83	.....	44.05	...	42.45	....	43.22
<hr/>									
C <sup>12</sup> H <sup>10</sup> O <sup>8</sup> .....	146	...	100.00	.....	100.00	...	100.00	....	100.00

*a*, *b*, and *c* were from two different preparations; *b* was not washed with water, but purified by simple rectification; *c* was the product *b* after washing with hot and cold water, and distillation.

The compound is metameric with biacetate of ethylene,  $C^4H^4, (C^4H^3O^2)^2, O^4$ .

Aldehyde heated with glacial acetic acid does not appear to unite with it.. (Geuther.)

Aldehyde appears to combine with benzoic and succinic anhydrides. (Geuther.)

*Compound of Aldehyde with Chloride of Acetyl.*  $C^4H^4O^2 + C^4H^3O^2Cl = C^8H^7ClO^4$ . — Produced by heating a mixture of aldehyde and chloride of acetyl to  $100^\circ$ , in a sealed tube for three hours. No gas is evolved on opening the tube; the contents distil over completely between  $90^\circ$  and  $140^\circ$ ; and by fractional distillation, the compound of aldehyde and chloride of acetyl is obtained, boiling between  $120^\circ$  and  $124^\circ$ . — It is lighter than water, and is decomposed by water, very slowly in the cold, more quickly when heated. It dissolves readily in dilute potash-ley, with formation of chloride of potassium and acetate of potash, and separation of aldehyde, which is partially resinized by the potash. With moist oxide of silver, it yields chloride and acetate of silver. (M. Simpson, *Compt. rend.* 47, 874; *Ann. Pharm.* 109, 156.)

					Simpson.			
8 C	.....	48.0	...	39.18	.....	38.65	...	38.98
7 H	.....	7.0	...	5.71	.....	5.68	...	5.77
Cl	.....	35.5	...	28.97	.....	28.00		
4 O	.....	32.0	...	26.14				
<hr/>								
C <sup>8</sup> H <sup>7</sup> ClO <sup>4</sup>	.....	122.5	...	100.00				

Isomeric with glycolic chloracetin (p. 432), and identical with the compound which Wurtz obtained by the action of chlorine on aldehyde (xii, 536), and regarded as produced by the substitution of 1 At. Cl for 1 At. H in a double molecule of aldehyde  $C^8H^8O^4$ . Simpson supposes that chloride of acetyl is first formed by the action of chlorine upon a portion of the aldehyde, and then unites with the remainder.

Page 281.

*Action of Sulphurous Acid Gas on Aldehyde. — Modifications of Aldehyde.* — Dry sulphurous acid gas passed into anhydrous aldehyde in a vessel surrounded with cold water, is rapidly absorbed, 11 pts. of aldehyde absorbing 19 pts. of the acid, whilst an increase of volume takes place.

The absorption-coefficient of aldehyde for sulphurous acid gas is 1.4 times as great as that of alcohol, and 7 times as great as that of water. No chemical combination appears to take place; as, on passing a stream of carbonic acid through the liquid at a slightly elevated temperature, all the sulphurous acid is expelled. (Geuther & Cartmell, *Proc. Roy. Soc.* 10, 111).

*Elaldehyde.* — When aldehyde saturated with sulphurous acid, is left for about a week at ordinary temperatures, in a well-stoppered bottle, it changes almost entirely into the solid and fusible modification, called elaldehyde. — To obtain this body pure, the liquid is mixed with as much water as is necessary to dissolve it; the acid is saturated by degrees with chalk; and the liquid is distilled as long as any drops pass into the receiver. The common aldehyde is separated in the resinous form by digestion with potash, and by repeated distillation, the elaldehyde may be obtained free from everything but a little water. (Geuther & Cartmell.)

Elaldehyde thus obtained, boils at  $124^\circ$ , and solidifies at  $10^\circ$ , starting into crystals, which likewise melt at  $10^\circ$ . Analysis shews that it is isomeric or polymeric with common aldehyde. It appears also to be identical with the modification which Weidenbusch obtained (viii, 277), by the action of sulphuric or nitric acid upon aldehyde, at low temperatures. This modification boiled at  $125^\circ$ , and solidified at low temperatures. Geuther and Cartmell are also of opinion, that the elaldehyde of Fehling (viii, 281) is likewise the same modification; but Fehling's product boiled at  $94^\circ$ , solidified at  $0^\circ$ , and melted again at  $2^\circ$ ; indeed, the only point in which it appears to agree with that obtained by Weidenbusch, is the vapour-density, which, as determined by Fehling, is 4.52, that of Weidenbusch's modification being 4.58.

### Acetic Acid.

**Occurrence.** Acetic acid is found in the so-called turpentine-water, which passes over, together with oil of turpentine, in the first stage of the dry distillation of pine-resin. This turpentine-water amounts to between 1 and 1½ per cent. of the resin, and contains from 10 to 11 per cent. of acetic acid (Chr. Grimm, *Ann. Pharm.* 107, 255).

**Formation.** Acetic acid is formed, together with other acids of the series,  $C^nH^nO^4$ ; in the putrefaction of yeast (A. Müller, *J. pr. Chem.* 71, 65; O. Hesse, *ibid.*, 471), and of wheat-flour (Sullivan, *Atlantis*, 1, 202); in the dry distillation of peat (Sullivan, *ibid.*, 185); in the germination of plants (Oudemans & Rauwenhoff, *Jahresber. d. Chem.* 1858, 493); and in the fermentation of diabetic urine (Klinger, *Ann. Pharm.* 106, 18). According to Neubauer (*Jahresber. d. Chem.* 1856, 712), acetic acid is the only acid formed in this last-mentioned process.

**Synthesis of Acetic Acid.** By the action of carbonic acid on sodium-methyl:



Carbonic acid gas was passed over sodium-methyl (prepared by the action of sodium on an ethereal solution of zinc-methyl, and mixed with zinc-methyl, zinc, sodium, and ether); the resulting solid mass was triturated with mercury, so as to convert the remaining free sodium into an amalgam, which would not decompose water so violently as pure sodium; and the product was distilled with excess of dilute sulphuric acid. An acid liquid then passed over, exhibiting distinctly the taste and odour of acetic acid. When redistilled and saturated with oxide of silver, it yielded a salt containing 64.00 and 64.88 p. c. silver, the formula  $C^4H^3AgO^4$ , requiring 64.67 p. c. — On saturating another portion of the acid liquid with carbonate of soda, and distilling the resulting soda-salt with arsenious acid, cacodyl was evolved in considerable quantity. (Wanklyn, *Ann. Pharm.* 111, 234.)

To show that the acetic acid did not result from the oxidation of the ether with which the sodium-methyl was mixed, another portion of this impure sodium-methyl was simply triturated with mercury as above, and then distilled with sulphuric acid; not the slightest trace of acetic acid could be detected in the distillate. (Wanklyn.)

**Acetates.** — The formation of acetic anhydride by the action of chloride of sulphur on acetates, first observed, Heintz (xii, 512), has been confirmed by Carius (*Ann. Pharm.* 106, 298), and by Schlagdenhauffen (*Compt. rend.* 48, 802).

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## Page 301.

*Acetonitrate of Baryta*,  $C^4H^3BaO^4, BaNO^5 + 8HO$ . — Obtained by dissolving an excess of nitrate of baryta in a hot concentrated solution of the acetate. Nitrate of baryta crystallizes out first, and the mother-liquor yields the double salt in large right rhombic prisms. (Lucius, *Ann. Pharm.* 103, 113.)

Dried at 160°.				Lucius.
2 BaO .....	153.2	...	59.33	59.23
4 C .....	24.0	...	9.30	9.34
3 H .....	3.0	...	1.16	1.59
3 O .....	24.0	...	9.30	
NO <sup>5</sup> .....	54.0	...	20.91	
<hr/>				
$C^4H^3BaO^4, BaNO^5$ ....	258.2	...	100.00	
Crystallized.				Lucius.
$C^4H^3BaO^4, BaNO^5$ .....	258.2	...	78.2	
8 HO .....	72.0	...	21.8	21.54
<hr/>				
$C^4H^3BaO^4, BaNO^5 + 8Aq$ ....	330.2	...	100.0	

*Acetonitrate of Strontia*,  $C^4H^3SrO^4, SrNO^5 + 3HO$ . — A solution of acetate and nitrate of strontia in equivalent proportions, yields this salt by spontaneous evaporation, in large limpid tabular crystals, permanent in the air; their formation is facilitated by the presence of a slight excess of acetic acid in the solution. (C. v. Hauer, *J. pr. Chem.* 74, 432).

## Page 304.

*Acetate of Alumina*. — A solution of gelatinous alumina in such a quantity of acetic acid, as to give the liquid a density of 8° or 9° Baumé, deposits, after standing for some weeks in a closed vessel, a more or less crystalline precipitate of acetate of alumina, containing  $Al^3O^3, 2C^4H^3O^3 + 6Aq$ . It is insoluble in water, sparingly soluble in dilute acids, readily in caustic alkalis. (C. Tissier, *Compt. rend.* 47, 931.)

## Page 308.

## Double Acetates of Uranium.

P. WESELSKY. *J. pr. Chem.* 75, 55.

These double salts are obtained by mixing the corresponding single salts in equivalent proportions, and recrystallizing with addition of acetic acid. Their general formula is  $MO, 2U^3O^3, 3C^4H^3O^3$  or  $C^4H^3MO^4, 2C^4H^3(U^3O^3)O^4$ , or  $C^4H^3(U^3M)O^{12}$  ( $U$ , denoting the monatomic radical  $U^3O^3$ , and  $M$  any other monatomic radical).

[For the crystalline forms and optical properties, see Grailich's *krystallographische Untersuchungen* S. 151.]

*Strontio-uranic Acetate* forms sulphur-yellow crystals, belonging to the square prismatic system. Gives off 10·06 p. c. (6 At.) water at 200°.

						Weselsky.	
2 U <sup>3</sup> O <sup>3</sup> .....	288·0	...	52·67	.....	53·08	...	52·76
SrO .....	51·8	...	9·47	.....	8·89		
3 C <sup>4</sup> H <sup>3</sup> O <sup>3</sup> .....	153·0	...	27·99				
6 HO .....	54·0	...	9·87				10·06
<hr/>							
C <sup>4</sup> H <sup>3</sup> SrO <sup>4</sup> , 2C <sup>4</sup> H <sup>3</sup> U <sub>1</sub> O <sup>4</sup> + 6Aq...	546·8	...	100·00				

*Calcio-uranic Acetate.* Sulphur-yellow crystals belonging to the right prismatic system. Ratio of the axes, 1:0·9798:0·389. Permanent in the air. Gives off its water at 200°.

					Weselsky.			
2 U <sup>2</sup> O <sup>3</sup> .....	288	...	53·23	.....	...	53·73	...	52·83
CaO.....	28	...	5·18	.....	5·57	...	5·35	
3 C <sup>4</sup> H <sup>3</sup> O <sup>3</sup> .....	153	...	28·28					
8 HO .....	72	...	13·31	.....	12·61			
<hr/>								
C <sup>4</sup> H <sup>3</sup> CaO <sup>4</sup> , 2C <sup>4</sup> H <sup>3</sup> U <sub>1</sub> O <sup>4</sup> + 8Aq....	541	...	100·00					

*Magnesio-uranic Acetate* crystallizes in the right prismatic system. Ratio of axes 1 : 0·6042 : 0·3960. The crystals exhibit dichroïsm in a much higher degree than those of uranic nitrate. They effloresce readily in the air, give off 6 At. water over oil of vitriol, and the rest when heated to 200°.

						Weselsky.	
2U <sup>3</sup> O <sup>3</sup> .....	288	...	50·62	.....	50·72		
MgO .....	20	...	3·51	.....	3·71		
3 C <sup>4</sup> H <sup>3</sup> O <sup>3</sup> .....	153	...	26·89				
12 HO .....	108	...	18·98	.....	19·18		
<hr/>							
C <sup>4</sup> H <sup>3</sup> MgO <sup>4</sup> , 2C <sup>4</sup> H <sup>3</sup> U <sub>1</sub> O <sup>4</sup> + 12Aq .....	569	...	100·00				

*Manganoso-uranic Acetate* crystallizes like the magnesia-salt, has a yellow colour, likewise effloresces very easily, and gives off all its water at 100°.

						Weselsky.	
2 U <sup>3</sup> O <sup>3</sup> .....	288·0	...	49·28	.....	48·60		
MnO .....	35·6	...	6·08	.....	5·88		
3 C <sup>4</sup> H <sup>3</sup> O <sup>3</sup> .....	153·0	...	26·17				
12 HO.....	108·0	...	18·47	.....	18·15		
<hr/>							
C <sup>4</sup> H <sup>3</sup> MnO <sup>4</sup> , 2C <sup>4</sup> H <sup>3</sup> U <sub>1</sub> O <sup>4</sup> + 12Aq .....	584·6	...	100·00				

*Zinco-uranic Acetate* forms sulphur-yellow crystals belonging to the right prismatic system, does not give off water when placed over oil of vitriol, but turns dingy grey, and gives off its water at 180°.

						Weselsky.	
2 U <sup>2</sup> O <sup>3</sup>	.....	288.0	...	52.88	.....	53.2	... 52.24
ZnO	.....	40.6	...	7.45	.....	...	... 6.24
3 C <sup>4</sup> H <sup>3</sup> O <sup>3</sup>	.....	153.0	...	28.09	.....		
7 HO	.....	63.0	...	11.58	.....		11.45
<hr/>							
C <sup>4</sup> H <sup>3</sup> ZnO <sup>4</sup> , 2C <sup>4</sup> H <sup>3</sup> U <sub>1</sub> O <sup>4</sup>	+ 7Aq.....	544.6	...	100.00			

*Cobalt-uranic Acetate* crystallizes like the zinc-salt, has a greenish-brown colour, which becomes darker at 100°. At 180°, it assumes a greyish violet colour, and gives off its water.

						Weselsky.	
2 U <sup>2</sup> O <sup>3</sup>	.....	288.0	...	53.18	.....	52.70	... 52.59 ... 53.79
CoO	.....	37.5	...	6.93	.....		6.40
3 C <sup>4</sup> H <sup>3</sup> O <sup>3</sup>	.....	153.0	...	28.25	.....		
7 HO	.....	63.0	...	11.64	.....		11.71
<hr/>							
C <sup>4</sup> H <sup>3</sup> CoO <sup>4</sup> , 2C <sup>4</sup> H <sup>3</sup> U <sub>1</sub> O <sup>4</sup>	+ 7Aq	541.5	...	100.00			

*Nickel-uranic Acetate* crystallizes like the zinc and cobalt salts, has an emerald green colour, and does not give off its water either in the air or over oil of vitriol. It becomes yellowish at 100°, and anhydrous at 180°.

						Weselsky.	
2 U <sup>2</sup> O <sup>3</sup>	.....	288.0	...	53.18	.....	52.05	... 53.04
NiO	.....	37.6	...	6.94	.....		11.71
3 C <sup>4</sup> H <sup>3</sup> O <sup>3</sup>	.....	153.0	...	28.25	.....		
7 HO	.....	63.0	...	11.63	.....		11.49
<hr/>							
C <sup>4</sup> H <sup>3</sup> NiO <sup>4</sup> , 2C <sup>4</sup> H <sup>3</sup> U <sub>1</sub> O <sup>4</sup>	+ 7Aq	541.6	...	100.00			

*Cadmio-uranic Acetate.* This salt differs in composition from all the preceding. It crystallizes like the magnesia-salt, and exhibits the same dichroism. Becomes somewhat opaque after long exposure to the air. At 180°, it melts in its water of crystallization, and becomes anhydrous.

						Weselsky.	
U <sup>2</sup> O <sup>3</sup>	.....	144	...	40.56	.....	40.10	... 40.62 ... 40.9
CaO	.....	64	...	18.03	.....		18.10
2 C <sup>4</sup> H <sup>3</sup> O <sup>3</sup>	.....	102	...	28.73	.....		
5 HO	.....	45	...	12.68	.....		13.56
<hr/>							
C <sup>4</sup> H <sup>3</sup> CaO <sup>4</sup> , C <sup>4</sup> H <sup>7</sup> U <sub>1</sub> O <sup>4</sup>	+ 5Aq.....	355	...	100.00			

*Basic Acetate of Lead.* — Litharge dissolves almost instantly in a solution of neutral acetate of lead, kept in a state of ebullition in a silver basin, and forms the basic acetate. (Rochleder, *J. pr. Chem.* 74, 28.)

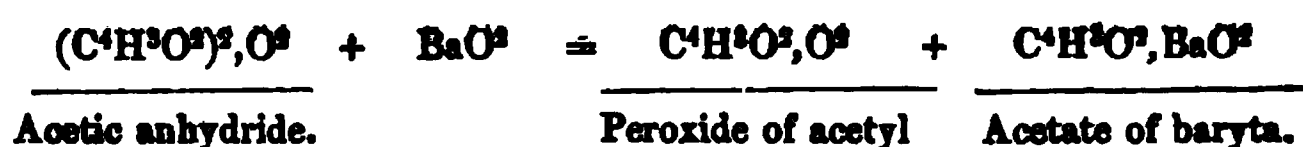


*Ferric Acetate.* — By dissolving the ferric oxide precipitated by ammonia (from a solution containing 1 pt. of iron), in 10 pts. of acetic acid of 30 p. c., at a temperature between 40° and 60°, and evaporating the decanted solution between 60° and 80°, an amorphous ferric acetate is obtained, which is soluble in water and alcohol, and is composed of  $\text{Fe}^3\text{O}^3, 2\text{C}^4\text{H}^3\text{O}^3 + \text{Aq.}$  (Oudemans, *Chem. Centr.* 1858, 486.)

### Peroxide of Acetyl. $\text{C}^4\text{H}^3\text{O}^3, \text{O}^3$ .

BRODIE. *Proc. Roy. Soc.* 9, 361.

Produced by the action of peroxide of barium on acetic anhydride:



The materials in equivalent proportions are very gradually mixed under anhydrous ether; the liquid is filtered from the acetate of baryta; the ether distilled off at a low temperature; and the remaining liquid well washed with water. Peroxide of acetyl then remains as a colourless viscid liquid, which has a pungent taste and burns the tongue like Cayenne pepper. A single drop placed upon a watch-glass and heated explodes with a loud report, shivering the glass to atoms. It is a powerful oxidizing agent, instantly decolorising sulphate of indigo, converting protoxide of manganese into peroxide, and ferrocyanide of potassium into ferricyanide. With baryta-water, it forms peroxide of barium and acetate of baryta.

*Peroxide of benzoyl*,  $\text{C}^{14}\text{H}^5\text{O}^3, \text{O}^3$ , is formed in like manner by the action of peroxide of barium on benzoic anhydride or chloride of benzoyl.



This acid, first obtained by Kekulé in 1854 by the action of penta-sulphide of phosphorus on glacial acetic acid (ix, 335), has been further

examined by Ulrich (*Ann. Pharm.* 109, 272), who has prepared several of its salts. Moreover, Jacquemin & Vosselmann (*Compt. rend.* 49, 371) have shown that it may also be obtained by the action of chloride of acetyl on sulphhydrate of potassium. When chloride of acetyl is added drop by drop to an equivalent quantity of the sulphhydrate contained in a retort furnished with a receiver, an energetic action immediately takes place, attended with the evolution of sufficient heat to volatilise a portion of the chloride of acetyl. On cohobating several times and distilling, a yellowish liquid is at length obtained, which retains only traces of chloride of acetyl. It distils almost wholly between  $90^{\circ}$  and  $100^{\circ}$ , and by fractional distillation a liquid is obtained boiling at  $93^{\circ}$ , and exhibiting the properties of thiactic acid described by Kekulé.

The process just described admits of generalisation, and may be applied to the preparation of the sulphuretted acids of all the acids of the series,  $C^nH^{2n}O^4$ , thus :



In like manner, by treating monosulphide of potassium with the chlorides of the radicals  $C^nH^{2n-1}O^3$ , the *sulphides* of the same radicals, homologous with thiactic anhydride, may be obtained,



Jacquemin & Vosselmann, by treating sulphide of potassium with chloride of acetyl, have obtained thiactic anhydride,  $(C^2H^3O^3)_2S^2$ , agreeing in all respects with the product which Kekulé prepared by the action of pentasulphide of phosphorus on acetic anhydride.

Respecting the preparation of thiactic acid by Kekulé's method, Ulrich gives the following details: 1 At. finely pulverized pentasulphide of phosphorus and 1 At. glacial acetic acid are mixed in a capacious retort and gently heated, the neck of the retort being directed upwards and connected with the lower end of a Liebig's condenser; sulphuretted hydrogen then escapes, arising from the action of the sulphide of phosphorus on the small quantity of water contained in the glacial acetic acid, and the mass is apt to froth over. After the action has continued for about two hours, the contents of the retort are distilled in the ordinary way. The reddish distillate is a mixture of thiactic acid, acetic acid and sulphur, and a black mass consisting of phosphorous acid and melted sulphur remains in the retort. By submitting the distillate to fractional distillation, pure thiactic acid is obtained, boiling at  $93^{\circ}$ . The product amounts to about one-fifth of the acetic acid employed.

*Properties.* Colourless liquid, having a pungent odour like that of acetic acid and sulphuretted hydrogen together. Soluble in water, especially in warm water, still more readily in alcohol and ether. Sp. gr. 1.074 at  $10^{\circ}$ . Boils at  $93^{\circ}$  (Kekulé), and distils unaltered. Does not solidify at  $-17^{\circ}$ .

Hence, by exposing the crude distillate of acetic and thiactic acid to a moderately low temperature, the greater part of the acetic acid may be separated at once.

The vapour-density determined at  $180^{\circ}$ , was found to be 2.465, the theoretical density (2 vol.) being 2.631. The difference arises from partial decomposition. Moreover, the vapour-density determined at

lower temperatures, comes out considerably greater, *e. g.* 3.04 at 125°, thiactic acid in this respect, resembling acetic acid. (Ulrich.)

*Decompositions.* The acid heated for some time to between 180° and 200°, in a sealed tube, suffers decomposition, the liquid as it cools, depositing crystals of sulphur, and sulphuretted hydrogen escaping when the tube is opened. On subsequently distilling the residual liquid, a fluid product goes over at 120°, having a peculiar odour, sinking in water, and being gradually decomposed thereby. It contains only 6 p. c. sulphur, whereas thiactic acid contains 27 p. c. It is perhaps, a mixture of acetyl,  $C^4H^3O^2$ , with undecomposed thiactic acid. — *Chlorine* decomposes thiactic acid with considerable rise of temperature, and formation of chloride of sulphur, hydrochloric acid, and chloride of acetyl. — *Oil of vitriol* decomposes it, with rise of temperature, evolution of sulphuretted hydrogen and sulphurous acid, and precipitation of sulphur. *Nitric acid* of sp. gr. 1.34, does not act upon it at ordinary temperatures, but at a gentle heat, it effects complete decomposition attended with explosion. Fuming nitric acid produces the same effect at ordinary temperatures. (Ulrich.)

*Combinations.* The *thiacetates*,  $C^4H^3MO^2S^2$ , are obtained by dissolving the oxides or carbonates in thiactic acid, or by decomposing the barium salt with sulphates. They are all more or less soluble in water and alcohol, and crystallize from the solutions; but they are less stable than the corresponding acetates.

*Thiacetate of Ammonia* is produced by passing dry ammonia-gas into thiactic acid dehydrated as completely as possible. Thick white fumes are formed, and the compound separates from the still liquid portion, in beautiful small white crystals, which are very deliquescent. (Ulrich.)

*Thiacetate of Potash* is easily obtained by adding thiactic acid to aqueous carbonate of potash, and evaporating over the water bath; it then separates in small colourless crystals, which may be purified by pressure and recrystallization. Dissolves readily in water and alcohol, and bears a heat of 100° without decomposition.

Ulrich.				
4 C .....	24.0	...	21.12	
3 H .....	3.0	...	2.64	
K .....	39.2	...	34.21	..... 34.25
2 S <sup>2</sup> .....	32.0	...	28.02	..... 27.60
2 O .....	16.0	...	14.01	
<hr/>				
$C^4H^3KO^2S^2$ .....	114.2	...	100.00	

*Thiacetate of Soda.*  $C^4H^3NaO^2S^2 + Aq$ , is prepared like the potash-salt, and crystallizes in small colourless and odourless crystals, which are very soluble in water and alcohol. Gave by analysis, 21.62 p. c. sodium, the formula requiring 21.49 p. c. This salt cannot be prepared by dissolving sodium in the acid, because the heat thereby evolved causes further decomposition and evolution of sulphuretted hydrogen. The aqueous solution of the resulting crystalline magma, yields on evaporation chiefly acetate of soda. (Ulrich.)

*Thiacetate of Baryta.*  $C^4H^3BaO^2S^2 + 3Aq.$  — When thiacetic acid is added to baryta-water, till a slight acid reaction is produced, and the liquid is then evaporated over the water-bath, the salt is obtained in colourless crystals, resembling those of heavy spar, and apparently belonging to the right prismatic system. It is purified by repeated crystallization. Dissolves in alcohol, and gives off part of its water at  $100^\circ$ . The solutions are neutral, and have a sweetish taste. (Ulrich.)

					Ulrich.
4 C.....	24.0	....	14.06	.....	13.71
6 H .....	6.0	....	3.52	.....	3.42
Ba .....	68.7	....	40.25	.....	39.86
2 S .....	32.0	....	18.74		
5 O.....	40.0	....	23.43		
<hr/> $C^4H^3BaO^2S^2 + 3Aq$ .....					
	170.7	....	100.00		

*Thiacetate of Strontia,*  $C^4H^3SrS^2O^2 + 2Aq.$  — Produced by treating strontia-water or the carbonate, with thiacetic acid, and separates from the aqueous solution in colourless crystals, belonging to the right prismatic system; bears a heat of  $120^\circ$ , without decomposition; gives by analysis 31.64 p. c. strontium, the formula requiring 32.01 p. c.

*Thiacetate of Lime,*  $C^4H^3CaO^2S^2 + 2Aq.$  — By decomposing the carbonate recently precipitated and suspended in water, with thiacetic acid, evaporating to dryness, and recrystallizing from water, the salt is obtained in colourless, inodorous crystals, which give off their water at  $100^\circ$ . The crystals give by analysis 19.69 p. c. calcium, the calculated quantity being 17.67.

*Thiacetate of Magnesia* is a viscid yellowish deliquescent mass, which cannot be made to crystallize.

*Thiacetate of Iron.* — Recently precipitated ferric hydrate dissolves somewhat freely in thiacetic acid, forming a solution which has a greenish colour, probably arising from reduction of the sesquioxide of iron to protoxide; the sulphur is not precipitated, but remains dissolved in the free thiacetic acid. On gently heating the liquid, sulphide of iron is precipitated. — A solution of sesquichloride of iron, mixed with a thiacetate, forms a clear solution, which gradually becomes turbid and deposits a scanty yellow precipitate; the decomposition is accelerated by heat.

*Mercuric Thiacetate.* — When thiacetic acid is poured upon dry mercuric oxide, the mass becomes so hot that part of the acid volatilizes, and the resulting mercury salt is partially decomposed, with formation of sulphide of mercury. — By precipitating a solution of mercuric chloride with thiacetate of potash, thiacetate of mercury is obtained as a copious white precipitate, which, however, soon turns black, from formation of sulphide of mercury.

*Thiacetate of Silver.* — The aqueous solution of thiacetate of potash, forms with nitrate of silver, a white insoluble silver-salt, which decomposes and blackens almost at the instant of formation. — Similarly with the copper salt. (Ulrich.)

lower temperatures, comes out considerably with aniline, the mixture thiactic acid in this respect, resembling ~~aniline~~, and a crystalline mass is

*Decompositions.* The acid heated  $\text{N}, \text{C}^4\text{H}^3\text{O}^2, \text{C}^{12}\text{H}^6, \text{H}$  (Analysis 69.45 C, and 6.66 H).  
 200°, in a sealed tube, suffers decomposition, depositing crystals of sulphur, and the tube is opened. On heating the fluid product goes over as water, and being gradually sulphur, whereas that of acetyl,  $\text{C}^4\text{H}^3\text{O}$ , decomposes thiactic acid of chlorid-  
 vitriol  
 hyd-  
 o.

Page 337.

*Sulphide of Ethyl,  $\text{C}^4\text{H}^6\text{S}^2$ .* The best mode of preparing this compound, is, according to Hobson (*Chem. Soc. Qu. J.* 10, 56), to distil the monosulphide of potassium in alcoholic solution with an equivalent quantity of sulphovinate of potash.  
 By treating sulphide of ethyl with dilute nitric acid, heating the solution over the water-bath till the excess of acid is expelled, saturating with carbonate of baryta, evaporating to dryness, exhausting the residue with alcohol, and concentrating the alcoholic extract, a small quantity of non-crystallizing syrupy liquid was obtained, containing sulphur, ethyl, and baryta, probably in the form of ethylotrithionate of baryta (xii, 514).

*Sulphide of Ethyl with Mercuric Iodide,  $\text{C}^4\text{H}^6\text{S}, \text{HgI}$ .*—Sulphide of ethyl does not unite directly with mercuric iodide as it does with the chloride (viii, 339). To prepare the iodine-compound, a mixture of alcohol, iodide of ethyl, and the chlorine-compound,  $\text{C}^4\text{H}^6\text{S}, \text{HgCl}$ , is heated for some hours to 100°, in a sealed tube; the contents then separate into two layers, the lower of which quickly aggregates into a yellow solid, while the upper, on cooling, yields the compound  $\text{C}^4\text{H}^6\text{S}, \text{HgI}$ , in the form of a yellow crystalline body. It is also obtained by heating to 100°, in a sealed tube, a mixture of finely pulverized mercuric sulphide with alcohol and iodide of ethyl. It may be purified by crystallization from boiling alcohol, in which it is sparingly soluble. — It has the aspect of sulphur; does not change colour when rubbed; melts at 110°; solidifies in a radio-crystalline mass on cooling; and is resolved at 100° into sulphide of ethyl and mercuric iodide. (A. Lori, *Compt. rend.* 46, 1280: *Ann. Pharm.* 107, 235.)

					Loir.
4 C .....	24	...	8.8	.....	8.25
5 H .....	5	...	1.8	.....	2.50
S .....	16	...	5.9	.....	6.40
Hg .....	100	...	36.7	.....	35.75
I .....	127	...	46.8	.....	47.90
<hr/>					
$\text{C}^4\text{H}^6\text{S}, \text{HgI}$ ....	272	...	100.0	.....	100.80

The corresponding *methyl*-compound  $\text{C}^3\text{H}^4\text{S}, \text{HgI}$ , may be obtained by precisely similar methods. It is yellow, melts at 87°, and decomposes at 165°. It gave by analysis 4.1 p. c. carbon, and 37.3 mercury, the formula requiring 4.6 C, and 38.7 Hg. (Loir.)

Page 358.

*Iodide of Ethyl.* — To prepare large quantities of iodide of ethyl without danger, De Vrij (*N. J. Pharm.* 31, 169) saturates anhydrous alcohol in a vessel surrounded with frigorific mixture, with dry hydrochloric acid gas; then determines the quantity of hydrochloric acid in a sample of the saturated liquid; and adds this liquid to the pulverized iodide of potassium contained in a retort, in quantity just sufficient to convert the iodide into chloride. The liquid is distilled off the next day, then washed and rectified.

*Iodide of methyl* may be prepared in like manner. On adding wood-spirit saturated with hydrochloric acid to iodide of potassium, decomposition takes place immediately, attended with great rise of temperature. (De Vrij.)

On the preparation of iodide of ethyl, see also Reynoso (*N. Ann. Chim. Phys.* 48, 385; *Jahresber d. Chem.* 1856, 565); and Walz (*N. Jahrb. Pharm.* 8, 274).

*Action of Iodide of Ethyl on Silver-salts.* — When iodide of ethyl is mixed in a closed vessel with *tungstate* of silver, strong action soon takes place, attended with rise of temperature, formation of iodide of silver, and ether, and separation of free tungstic acid. No tungstate of ethyl is produced. (Gössmann, *Ann. Pharm.* 101, 218.) Similar results are obtained with *molybdate*, *arsenite*, *arsenate*, *antimonate*, *stannate*, *borate* and *tellurate* of silver. When iodide of ethyl is enclosed in sealed tubes, with *bichromate* of silver, a small quantity of aldehyde is formed. The mixture becomes very hot, and the tubes are very liable to burst. — Iodide of ethyl, heated to 100° for some hours in sealed tubes with *sulphide*, *sulphate*, or *sulphocyanide* of silver, is converted into sulphide, sulphate, or sulphocyanide of ethyl. (Nason, *Ann. Pharm.* 104, 126).

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*Bromide of Ethyl* is easily prepared by distilling 4 pts. of pulverized bromide of potassium, with 5 pts. of a mixture of 2 pts. of oil of vitriol and 1 pt. of 96 per cent alcohol. (De Vrij.) See also Reynoso (*loc. cit.*).

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Page 366.

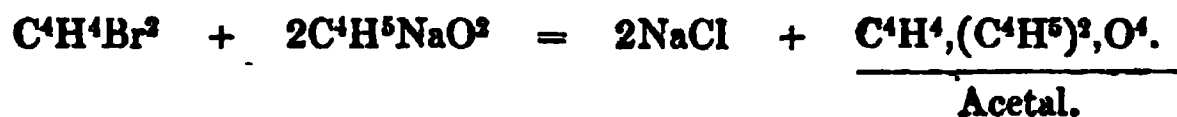
### Bromide of Ethylidene. $C^2H^4Br^2$ .

WURTZ & FRAPOLLI. *Ann. Pharm.* 108, 225.

Obtained by passing vapour of aldehyde over pentabromide of phosphorus in a vessel externally cooled. The products formed are bromide of ethylidene and oxybromide of phosphorus, which cannot be separated by fractional distillation, because the bromide of ethylidene is decomposed by heat. The oxybromide of phosphorus may however be removed

by agitating the mixture with lumps of ice, replacing them as they melt. A dense yellow liquid is thus obtained, which is insoluble in water and is readily decomposed by water, with evolution of hydrobromic acid: hence it is impossible to obtain the compound in a state of sufficient purity for analysis.

Bromide of ethylidene treated with ethylate of sodium yields acetal:



The acetal thus produced yielded by analysis 61.2 p.c. carbon and 12.1 hydrogen, the formula  $\text{C}^{12}\text{H}^{14}\text{O}^4$  requiring 61.02 C and 11.86 H.

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Page 376.

### Chloride of Ethylidene. $\text{C}^4\text{H}^4\text{Cl}^2$ .

GEUTHER. *Ann. Pharm.* 105, 321.

WURTZ & FRAPOLLI. *Compt. rend.* 47, 418; *Ann. Pharm.* 108, 223.

Produced by the action of pentachloride of phosphorus upon aldehyde:



[By the action of  $\text{PCl}^5$  on glycol, the isomeric compound chloride of ethylene is produced (p. 423)].

The vessel containing the chloride of phosphorus must be kept cool, while the aldehyde is added by small portions; afterwards the mixture is warmed, whereupon the whole dissolves to a homogeneous liquid, which gradually blackens when distilled, and gives off below  $100^\circ$ , a liquid from which water separates an oily body, and above  $100^\circ$ , oxychloride of phosphorus. The oily liquid, dried by chloride of calcium and rectified, yields chloride of ethylidene.

Transparent, colourless, oily liquid, resembling chloroform in taste and odour. Sp. gr. 1.189 at  $4.3^\circ$  (Geuther). Boils at  $58^\circ$  (Wurtz & Frapoli); at  $60^\circ$  (Geuther).

					Geuther.
4 C	.....	24	...	24.24	..... 24.44
4 H	.....	4	...	4.04	..... 4.47
2 Cl	.....	71	...	71.72	..... 71.55
<hr/>					
$\text{C}^4\text{H}^4\text{Cl}^2$	.....	99	...	100.00	..... 100.46

Isomeric with chloride of ethylene, but differs from it in specific gravity and in boiling point, the sp. gr. of chloride of ethylene being 1.256 at  $12^\circ$  according to Regnault, and the boiling point  $86^\circ$  according to Dumas. The two bodies differ also in their behaviour with alcoholic potash, chloride of ethylene being easily decomposed thereby, into chloride of potassium and the compound  $\text{C}^4\text{H}^3\text{Cl}$ ; whereas chloride of ethylidene is not all affected by alcoholic potash in the cold, and with difficulty even when heated.



Chloride of ethylidene treated with ethylate of sodium does not act like the bromide and produce acetal (p. 452), but yields a chlorinated gas,  $C^4H^3Cl$ , identical in composition and properties with the so-called *chloride of acetyl* (chloride of *acetosyl* or *vinyl*, ix, 191), derived from Dutch liquid. The identity of the two gases is shown by their solubility in water and alcohol, and by their behaviour with chlorine; 1 vol. water at  $25^\circ$  absorbed 0.81 vol. of the gas (*A*) obtained as above from chloride of ethylidene, and the same volume of the gas (*B*) from chloride of ethylene. 1 vol. anhydrous alcohol at  $22.5^\circ$  dissolved 55.1 vol. of the gas *A*, and at  $22.9^\circ$ , 54.5 vol. of the gas *B*. The gas *A* absorbs chlorine and forms a compound  $C^4H^3Cl^3$ , identical with that which Regnault obtained in like manner from the gas *B*.

The term *ethylidene* is applied to a radical ( $C^2H^4$ ), supposed to exist in a series of compounds derived from aldehyde, and isomeric with the ethylene-compounds, which are derivatives of glycol, *e. g.* chloride of ethylidene, isomeric with chloride of ethylene; aldehyde with oxide of ethylene; Geuther's compound of aldehyde and acetic anhydride, with biacetate of ethylene; the compound of aldehyde and chloride of acetyl, ( $C^4H^4O^2, C^4H^3O^2Cl$ ), with glycolic chloracetin; and acetal with biethylglycol. These two series of compounds are intimately related to each other, and the compound  $C^4H^3Cl$ , which may be produced, from either of them, may be regarded as the link between the two. (Wurtz and Frapoli).

The so-called ethylidene-compounds may, however, be viewed in a different light, viz., as containing the radical  $C^4H^3$ . At all events, chloride of ethylidene, as pointed out by Beilstein (*Bull. Soc. Chim. de Paris*, i, 60), appears to be identical with Regnault's *monochlorinated hydrochloric ether*,  $C^4H^3Cl, HCl$  (viii, 375), that compound having a specific gravity of 1.174 at  $17^\circ$ , boiling at  $64^\circ$ , and being also with difficulty acted upon by alcoholic potash.

### Oxychloride of Ethylidene. $C^8H^8Cl^2O^2$ .

A. LIEBEN. *Compt. rend.* 46, 662; *Ann. Pharm.* 106, 336.

Produced by the action of hydrochloric acid on aldehyde:



When aldehyde cooled by a freezing mixture is saturated with dry hydrochloric acid gas, the liquid increases in volume and separates into two colourless layers, which must be immediately separated, as they act upon each other. The lower layer is aqueous hydrochloric acid, the upper is oxychloride of ethylidene, which may be purified by repeated distillation over chloride of calcium.

Transparent, colourless liquid, smelling of aldehyde and hydrochloric acid. Sp. gr. 1.1376 at  $12^\circ$ . Boiling point  $116^\circ$ — $117^\circ$ . Vapour-density 5.08 (taken at  $173^\circ$ ).

						Lieben.	
8 C	.....	48	....	33.57	.....	33.46	.... 33.41
8 H	.....	8	....	5.59	.....	5.77	.... 5.81
2 Cl	.....	71	....	49.65	.....	49.12	
2 O	.....	16	....	11.19	.....	11.65	
<hr/>							
$C^8H^8Cl^2O^2$	.....	143	....	100.00	.....	100.00	



	Vol.	Density.
O-vapour.....	8 .....	3.3280
H-gas .....	8 .....	0.5544
Cl-gas .....	2 .....	4.9086
O-gas .....	1 .....	1.1093
<hr/>		
Vapour of $C^8H^8Cl^2O^2$ .....	2 .....	9.9003
	1 .....	4.9501

May be regarded as a double molecule of aldehyde in which 2 At. O are replaced by 2 At. Cl. Isomeric with D'Arcet's chlorethral (ix, 192).

Oxychloride of ethylidene is not decomposed by water in the cold, but on heating, it is converted thereby into hydrochloric acid and aldehyde. — Pentachloride of phosphorus does not act upon it at ordinary temperatures, but is completely dissolved when heated with it in a sealed tube to  $100^\circ$  for several hours: the organic product cannot however be separated from the oxychloride of phosphorus formed at the same time. (Wurtz & Frapelli.)

Geuther & Cartmell, by treating aldehyde with hydrochloric acid, have obtained, besides the oxychloride just described, another which has the composition  $C^{12}H^{12}Cl^2O^4$ , and may be regarded as a triple molecule of aldehyde  $C^4H^4O$ , in which 2 At. O are replaced by 2 At. Cl. (*Proc. Roy. Soc.* 10, 110).

### Chlorethylate of Ethylidene.



WURTZ & FRAPOLLI. *Ann. Pharm.* 108, 226.

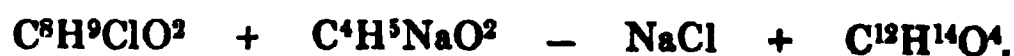
Produced by passing hydrochloric acid to saturation into a mixture of 1 vol. aldehyde and 2 vol. absolute alcohol surrounded with a freezing mixture. Two layers of liquid are then formed, the lower consisting of aqueous hydrochloric acid and the upper ethereal layer of chlorethylate of ethylidene:



					Wurtz & Frapelli.
8 C .....	48.0	....	44.24	.....	45.14
9 H .....	9.0	....	8.29	.....	9.51
Cl .....	35.5	....	32.72	.....	30.34
2 O .....	16.0	....	14.75	.....	15.01
<hr/>					
$C^8H^8ClO^2$ .....	78.5	....	100.00	.....	100.00

The differences between the analytical and calculated results arise from partial decomposition during distillation. The carbon and hydrogen were determined from a specimen boiling between  $95^\circ$  and  $97^\circ$ ; the chlorine from one which boiled at about  $98^\circ$ .

This compound, treated with ethylate of sodium, yields chloride of sodium and acetal:



The acetal thus produced yielded by analysis 61.36 and 60.80 p.c. carbon; and 12.40 and 12.36 hydrogen. This method of converting aldehyde into acetal is much easier than that which requires the preparation of bromide of ethylidene, the latter compound being very difficult to obtain.

### Chlorosulphate of Ethyl. $\text{C}^4\text{H}^5\text{Cl}, \text{S}^2\text{O}^6$ .

R. WILLIAMSON. *Chem. Soc. Qu. J.* 10, 100.

Produced by the action of chloride of ethyl on anhydrous sulphuric acid. — When a thin glass vessel containing the anhydrous acid is enclosed in a sealed tube containing chloride of ethyl, and the tube is shaken so as to break the inner vessel, the anhydride dissolves in the chloride of ethyl; and on subsequently distilling off the excess of chloride of ethyl, the chlorosulphate remains in the form of a colourless oily liquid. — It appears also to be formed by the action of chlorosulphuric acid on absolute alcohol:



It sinks in water, and is slowly decomposed thereby, yielding hydrochloric, sulphuric, and probably also ethylsulphuric acid.

R. Williamson.									
$\text{S}^2\text{O}^6$ .....	80.0	...	55.36	.....	54.6	...	55.4	...	56.1
$\text{C}^4\text{H}^5\text{Cl}$ .....	64.5	...	44.64	.....	45.4	...	44.6	...	43.9
<hr/>									
$\text{C}^4\text{H}^5\text{Cl}, \text{S}^2\text{O}^6$ ....	144.5	...	100.00	.....	100.0	...	100.0	...	100.0

This compound may be regarded as  $\text{S}^2\text{O}^4 \left\{ \begin{smallmatrix} \text{C}^4\text{H}^5\text{O}^2 \\ \text{Cl} \end{smallmatrix} \right.$ , that is to say as sulphuric acid  $\text{S}^2\text{O}^4 \left\{ \begin{smallmatrix} \text{HO}^2 \\ \text{HO}^2 \end{smallmatrix} \right.$  in which 1 At. H is replaced by ethyl and 1 At.  $\text{HO}^2$  by Cl. It is a homologue of the *chlorohydrated sulphuric acid*  $\text{S}^2\text{O}^4 \left\{ \begin{smallmatrix} \text{HO}^2 \\ \text{Cl} \end{smallmatrix} \right.$ , which A. W. Williamson obtained (*Chem. Soc. Qu. J.* 7, 180) by the action of sulphuric acid on pentachloride of phosphorus. This latter compound may also be produced by the direct combination of hydrochloric acid with sulphuric anhydride.

A similar compound is formed with *chloride of methyl*.

*Chloride of acetyl*,  $\text{C}^4\text{H}^3\text{O}^2\text{Cl}$ , likewise acts on anhydrous sulphuric acid in closed vessels, with evolution of heat, and formation of a liquid which is colourless at first, but afterwards turns yellow and red, and decomposes rapidly in contact with the air. When dropped into water, it sinks to the bottom and gradually dissolves, forming an acid liquid, which forms with baryta a soluble salt, yielding a gelatinous precipitate on the addition of an alkali. (R. Williamson.)

The *chlorosulphate of phenyl*,  $\text{C}^{12}\text{H}^5\text{Cl}, \text{S}^2\text{O}^6$  (chlorosulphobenzolic acid), obtained by Hutchings (xi, 175), is likewise a compound of similar constitution.

Page 399.

*Ethylphosphoric Acid.* — According to Reynoso (*N. Ann. Chim. Phys.* 48, 385), the action of iodine and phosphorus upon alcohol (as in the preparation of iodide of ethyl), is represented by the equation ;



The formation of ethylphosphoric acid in this process has been confirmed by Tuttle (*Ann. Pharm.* 101, 290). On diluting with water the syrupy liquid which remains after distilling off the iodide of ethyl, neutralizing with carbonate of baryta, and precipitating with alcohol, a salt was obtained which, after drying at 100°, yielded 57·9 p. c. of baryta; agreeing nearly with the formula  $\text{PO}^3, \text{C}^4\text{H}^6, \text{Ba}^2$ , which requires 58·3 per cent.

Page 475.

*Nitrate of Ethyl.* When 1 At. iodide of potassium, and 1 At. nitrate of ethyl are heated, together with an equal volume of alcohol, to 100°, in a sealed tube, iodide of ethyl is formed, together with a little ether, and a separation of iodine takes place. The essential part of the reaction is expressed by the equation :



The ether appears to result from the action of the iodide of ethyl on the alcohol ; and the iodine, together with some gaseous products, likewise results from secondary decompositions. (Juncadella, *Compt. rend.* 48, 345.)

Page 486.

### Compounds of Cyanide of Ethyl with Chlorides.

W. HENKEL. *Ann. Pharm.* 106, 282.

These compounds are formed by direct combination, which is often attended with so great a rise of temperature, that external cooling is necessary to prevent decomposition. Many of them crystallize well, and may be distilled without decomposition ; but they are instantly decomposed by alcohol and water, and cannot be recrystallized from ether ; hence they are difficult to purify.

*Cyanide of Ethyl with Chloride of Titanium.*  $\text{C}^6\text{H}^5\text{N}, \text{TiCl}^3$ . — The two substances unite without much rise of temperature, and on agitation, the compound separates in snow-white crystalline crusts, which distil without decomposition.

	Calculated.	Found.
Titanium .....	57.10 .....	58.21 p.c.

*With Pentachloride of Antimony.*  $\text{C}^6\text{H}^5\text{N}, \text{SbCl}^5$ . — The heat evolved by the combination is so great, that to prevent blackening and decomposition, it is necessary to cool the retort with a mixture of snow and salt. On distilling off the excess of cyanide of ethyl, the compound separates as a yellow mass, which cannot be sublimed without decomposition.

	Calculated.	Found.
Antimony .....	35.68 .....	34.59 and 35.26 p.c.

*With Bichloride of Tin.*  $\text{C}^6\text{H}^5\text{N}, \text{SnCl}^2$ . — The most stable of this class of compounds.

	Calculated.	Found.
Sn .....	25.00 .....	25.47
Cl .....	30.64 .....	30.37

The crystals, when left to stand on a porous tile over oil of vitriol, give off a considerable quantity of cyanide of ethyl. They were afterwards found to contain 37.9 p. c. tin.

*With Terchloride of Gold.*  $\text{C}^6\text{H}^5\text{N}, \text{AuCl}^3$ . — Resembles the corresponding methyl-compound (p. 412).

	Calculated.	Found.
Gold .....	42.38 .....	41.13

*With Bichloride of Platinum.*  $\text{C}^6\text{H}^5\text{N}, \text{PtCl}^2$ . — Resembles the preceding.

	Calculated.	Found.
Platinum .....	42.84 .....	43.92

*With Chloride of Carbonyl.*  $\text{C}^6\text{H}^5\text{N}, \text{C}^2\text{O}^2\text{Cl}^2$ . — Phosgene gas prepared by passing carbonic oxide through boiling pentachloride of antimony, and freed from the vapours of the latter compound by passing through a strongly cooled receiver, was introduced into a tube containing cyanide of ethyl, and cooled with snow. The product is a transparent colourless liquid, which, in contact with water, gives off a considerable quantity of gas burning with a blue flame.

	Calculated.	Found.
Chlorine .....	46.1 .....	45.78

*With Chloride of Cyanogen.*  $C^6H^6N,CyCl$ . — Obtained by passing dry gaseous chloride of cyanogen, for a long time through cyanide of ethyl. — Colourless liquid, which boils between  $60^\circ$  and  $68^\circ$ , irritates the eyes and respiratory organs strongly, and is decomposed, with rise of temperature by contact with water.

	Calculated.	Found.
Chlorine.....	30.47	29.86

It decomposes spontaneously in a few days, the whole of the chloride of cyanogen being separated in the solid form, as  $Cy^3Cl^3$ . (Hencke.)

*Cyanide of Ethyl and Silver.* — When iodide of ethyl and cyanide of silver, in equivalent quantities are heated together to  $100^\circ$  in a sealed glass tube, a viscid oil is formed, which solidifies to a crystalline mass on cooling, and contains, together with iodide of silver, a compound of cyanide of ethyl and cyanide of silver, which does not yield pure cyanide of ethyl by distillation. On distilling it with water, a liquid is obtained which smells strongly of cyanide of ethyl, and when mixed with an acid and evaporated, yields an impure salt of ethylamine.

When a mixture of cyanide of silver, iodide of ethyl, and water, is heated to  $100^\circ$ , till the half-fused mass no longer gives off bubbles of iodide of ethyl, the aqueous solution yields on cooling, fine shining crystals of the compound  $AgCy,C^4H^5Cy$ . This substance may be obtained in larger quantity, by repeatedly boiling with water the fused product resulting from the decomposition of cyanide of silver by iodide of ethyl, and quickly drying upon paper the crystals which separate on cooling. They are microscopic square prisms, which have a very unpleasant odour, melt between  $80^\circ$  and  $90^\circ$ , blacken quickly in the moist state, and are very slightly soluble in alcohol and ether. When exposed for some time to the air, they lose their odour, and are decomposed, cyanide of silver remaining in the form of the original crystals. — When distilled with potash, they yield a liquid which smells of cyanide of ethyl, and when treated with hydrochloric acid, yields a pure salt of ethylamine. — But if the aqueous solution of the product obtained by decomposing cyanide of silver with iodide of ethyl, be treated with dilute sulphuric [hydrochloric?] acid, hydrocyanic and carbonic acids are evolved, cyanide of silver is precipitated, and the evaporated liquid contains, together with ethylamine, a body which emits the odour of cyanide of ethyl when boiled with potash, and is perhaps a compound of hydrochloric acid with cyanide of ethyl  $HCl,C^6H^6N$ , the latter playing the part of a base. (E. Meyer, *J. pr. Chem.* 68, 279.)

### Platinocyanide of Ethyl.



C. v. THANN. *Ann. Pharm.* 107, 315.

Prepared by passing dry hydrochloric acid gas into a solution of hydroplatinocyanic acid in absolute alcohol. The gas is rapidly absorbed, the liquid becomes very hot and solidifies on cooling to a crystalline pulp, composed of small aurora-red needles. The crystals must be quickly filtered and dried with great care over oil of vitriol and caustic potash.

The crystals thus obtained contain 2 At. water, from which they cannot be separated without decomposition. They belong to the right prismatic system, and are combinations of a prism with the basic terminal face and a pyramid. They appear to be isomorphous with platinocyanide of potassium. Under the microscope, the body of the crystal exhibits a brown colour, while the surface varies from light azure to dark steel-blue.

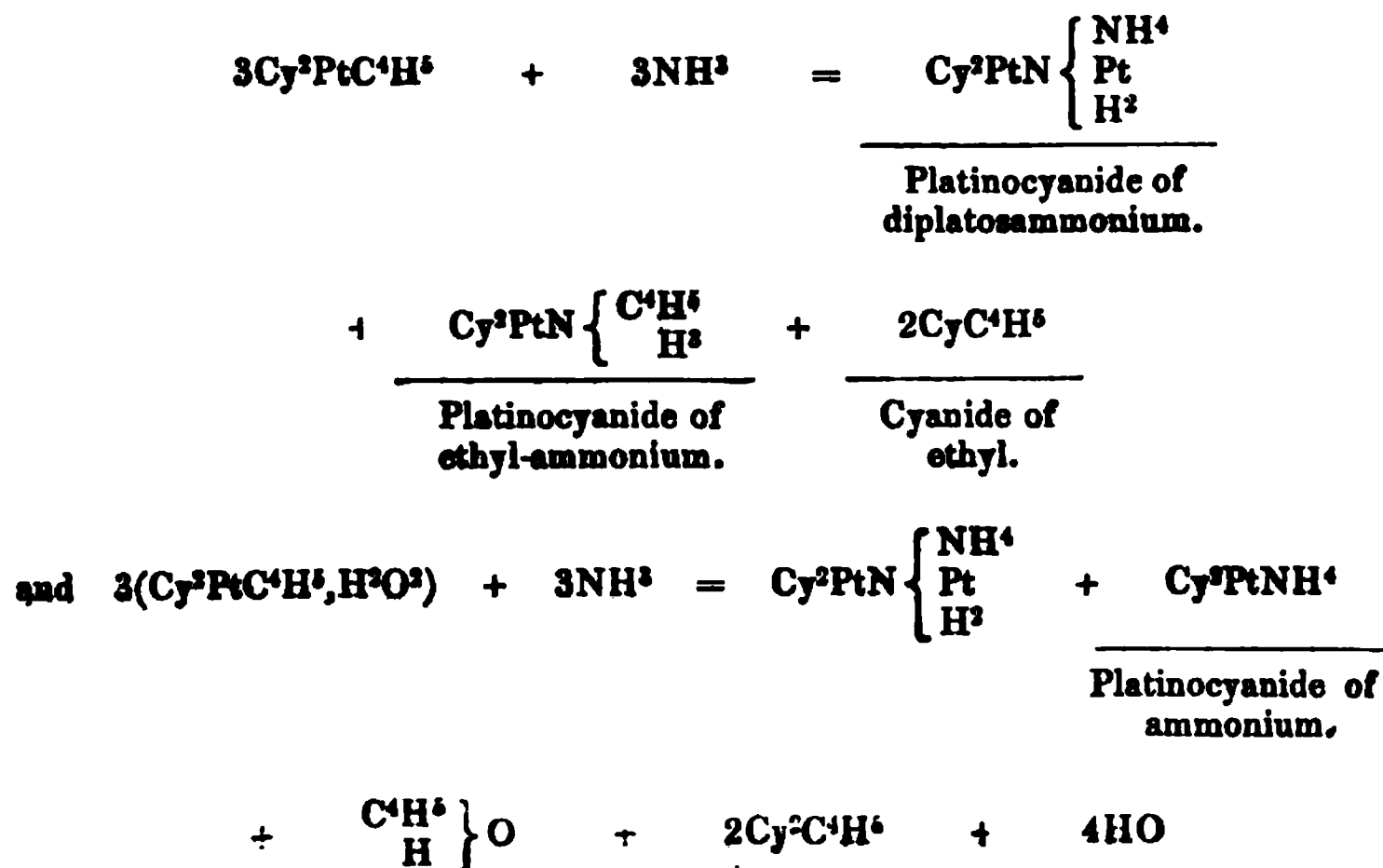
v. Thann.									
8 C	.....	48	.....	24.24	.....	22.72	....	....	24.33
2 N	.....	28	.....	14.14	.....	....	14.09	....	....
7 H	.....	7	.....	3.54	.....	3.64	....	....	3.79
[Pt	.....	99	.....	50.00	.....	49.45	....	....	50.07
2 O	.....	16	.....	8.08	.....	.....	.....	.....	.....
<hr/>									
PtC <sup>4</sup> H <sup>6</sup> Cy <sup>2</sup> + 2HO...	198	.....	100.00						

The deficiency of carbon in some of the analyses is due to the great tendency of the compound to decompose.

Hydrated platinocyanide of ethyl is resolved at 100°, into alcohol and hydroplatinocyanic acid:



It suffers the same decomposition in contact with water. At higher temperatures, it is resolved into platinous cyanide, cyanide of ethyl and water. Aqueous ammonia added in excess to a concentrated alcoholic solution of platinocyanide of ethyl mixed with 4 or 5 times its bulk of ether, forms stellate groups of needles consisting of platinocyanide of diplatosammonium (viii, 45); and on evaporating the mother-liquor to dryness, dissolving it in alcohol, and leaving the solution to evaporate over oil of vitriol, it first deposits *hydrated platinocyanide of ammonium*, and then yellow needles probably consisting of *platinocyanide of ethyl-ammonium*. The decomposition may be represented by the equation ;



Probably both these reactions go on together; but the cyanide of ethyl appears to be further acted on by the free ammonia, perhaps yielding ethylamine and cyanide of ammonium:



On saturating the ammoniacal distillate with hydrochloric acid, evaporating to dryness, treating the residue with a mixture of absolute alcohol and ether, and again evaporating, a hygroscopic residue was left containing 61.8 p. c. chlorine, probably therefore a mixture of sal-ammoniac (66.4 p. c. Cl) and chloride of ethyl-ammonium (42.9 p. c. Cl).

Dry ammonia gas converts platinocyanide of ethyl into platinocyanide of ammonium and ethylamine;



The volatile products being condensed in hydrochloric acid and the solution treated as above, a residue was obtained containing 6.4 p. c. chlorine.

*Platinocyanide of Ethylammonium*,  $\text{Cy}^2\text{Pt}, (\text{N}, \text{H}^3, \text{C}^4\text{H}^5)$ . — The yellow crystals obtained in the manner above described, by the action of aqueous ammonia on a solution of platinocyanide of ethyl in alcohol and ether, dissolve very readily in water and alcohol; and the solutions evaporated in the air, leave long yellow needles, which, while immersed in the mother-liquor, exhibit a splendid violet iridescence on the surface. They gave by analysis 50.98 p. c. platinum, the above formula requiring 50.26 p. c. (v. Thann.)

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Page 489.

*Sulphocyanide of Ethyl*. — Ammonia in the state of gas, does not act upon sulphocyanide of ethyl; but in alcoholic solution it separates a black-brown substance, especially if the mixture is heated. When sulphocyanide of ethyl is heated for several days to 100°, in a sealed tube with strong aqueous ammonia, a black substance (A) separates, which is volatile for the most part when strongly heated, sparingly soluble in water, alcohol and ammonia, easily and with dark colour in the fixed alkalis, from which solutions it is partially deposited after awhile. When analyzed without further purification, it gave 41.1 p. c. carbon, 8.9 hydrogen, and 41.5 nitrogen.

The brown aqueous solution from which the black substance was deposited, contained (together with free ammonia) cyanide of ammonium, carbonate of ammonia, oxalate of ammonia, and urea; bisulphide of ethyl  $\text{C}^4\text{H}^5\text{S}^2$ , was likewise formed. It appears then that the sulphocyanide of ethyl  $\text{C}^4\text{H}^5, \text{C}^2\text{NS}^2$ , gives up  $\text{C}^2\text{N}$ , leaving  $\text{C}^4\text{H}^5\text{S}^2$ , and the cyanogen thus separated reacts further on the ammonia. (A. Kremer, *J. pr. Chem.* 73, 265.)

*Sulphocyanide of amyl* is decomposed by ammonia in a similar manner, but less easily. (Kremer.)

Sulphocyanide of ethyl heated for several days to  $100^{\circ}$ , in sealed glass tubes, with aqueous *potash*, is converted into bisulphide of ethyl, with simultaneous formation of cyanide and cyanate of potassium:



The separation of cyanogen in this decomposition, and the decomposition of the resulting cyanate of potash, explain Lowig's statement (viii, 390), that sulphocyanide of ethyl boiled with alcoholic potash yields bisulphide of ethyl, ammonia, and carbonate of potash. (Brüning, *Ann. Pharm.* 104, 198.)

*Sulphocyanide of Ethylene*,  $\text{C}^4\text{H}^4, (\text{C}^2\text{NS}^2)^2$ . — Formation and preparation (x, 520). The compound melts at  $90^{\circ}$ , and solidifies at  $83^{\circ}$ .

					Buff.
8 C	.....	48	.....	33.33	..... 32.86
4 H	.....	4	.....	2.75	..... 2.89
2 N	.....	28	.....	19.44	..... 19.43
4 S	.....	64	.....	44.48	..... 44.80
<hr/>					
$\text{C}^4\text{H}^4, (\text{C}^2\text{NS}^2)^2$	....	144	.....	100.00	..... 99.98

In very dilute nitric acid it dissolves readily with the aid of heat, and crystallizes out unchanged on cooling; but stronger nitric acid decomposes it, forming a crystalline acid, probably bisulphetholic acid (xii, 516). (Buff, *Ann. Pharm.* 100, 229.)



# ADDITIONS TO VOL. IX.

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Page 1.

## Acetone.

- FRIEDEL. *Compt. rend.* 46, 1165; 47, 921. *Bull. Soc. Chim. de Paris* 1, 26, 57. *Ann. Pharm.* 107, 174; 112, 236.  
RICHE. *Compt. rend.* 49, 176. *Bull. Soc. Chim. de Paris* 1, 29. *Chem. Gaz.*, 1859, 323.  
FITTIG. *Ann. Pharm.* 110, 23.  
STÄDELER. *Ann. Pharm.* 111, 277.

*Constitution of Acetone.* — From Friedel's experiments it appears that when a mixture of acetone and water acidulated with sulphuric acid, is subjected to the action of a feeble current of electricity, the acetone is oxidised by oxygen derived from the water, and converted partly into acetic, partly into formic acid, probably according to the equation:



This result affords an additional argument in favour of the theory which regards acetone as a methyl-compound  $\text{C}^4\text{H}^3\text{O}^2, \text{C}^2\text{H}^3$ . — Carbonic acid is also produced, but it is probably due, either to secondary reactions, or to a more complete combustion of a portion of the acetone:  $\text{C}^6\text{H}^6\text{O}^2 + 6\text{O} = 6\text{CO}^2 + 6\text{HO}$ . (*Bull. Soc. Chim. de Paris*, i, 57.)

The same conclusion may be drawn from the electrolysis of a mixture of acetone and nitric acid. When a weak current (from 3 Bunsen's cells) is passed for four or five days through a mixture of 2 pts. acetone, 1 pt. water, and 1 pt. ordinary nitric acid; the liquid afterwards saturated with carbonate of potash, and the resulting salt treated with alcohol, acetate of potash is dissolved. Moreover, the crude salt obtained by saturating the acid, gives off, when heated with potash, alkaline vapours consisting of ammonia and methylamine. The ammonia is formed by the union of the nascent hydrogen and nitrogen resulting from the decomposition of the aqueous nitric acid; and the presence of methylamine is an indication that the acetone contains methyl. — A small quantity of oxamide is sometimes produced, probably by a secondary reaction (Riche, *Compt. rend.* 49, 179).

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## Page 4.

**CHLORINATED ACETONES.** — The series of these compounds is now complete. *Monochloracetone*  $C^6H^5ClO^2$ , is produced by the electrolysis of a mixture of acetone and hydrochloric acid (Riche, *loc. cit.*) — *Bichloracetone* (Kane's mesitic chloral, ix, 27) is produced by the action of chlorine-gas upon acetone. — *Ter-* and *quadro-chloracetone* were obtained by Bouis (ix, 262) by passing chlorine-gas into wood-spirit (probably containing acetone). The so-called *methylic chloral*  $C^{12}H^8Cl^6O^5$ , which Weidmann & Schweizer obtained by the action of chlorine on wood-spirit (vii, 261), was also probably a hydrated mixture of bi- and ter-chlorinated acetone:



*Pentachloracetone*,  $C^6HCl^5O^2$ , is obtained by the action of a mixture of hydrochloric acid and chlorate of potash on various organic compounds, viz., kinic, citric, gallic, pyrogallie, catechucic, and salicylic acids, also kinone, indigo, tyrosin, albumen, and muscular flesh (Städeler); and *hexachlorinated acetone*,  $C^6H^0O^2$ , is probably the compound which Plantamour obtained by the action of chlorine on nitric acid in sunshine (ix, 5; xii, 440).

**Monochloracetone.**  $C^6H^5ClO^2$ . — When a feeble current of electricity (from three Bunsen's cells) is passed through a mixture of acetone and hydrochloric acid, the latter compound is decomposed by the current, and hydrogen is abundantly evolved at the negative pole; but the chlorine at the positive pole, instead of escaping in the gaseous form, acts energetically on the acetone and forms a substitution-product. The liquid, which is clear at the commencement of the action, soon becomes turbid, in consequence of the formation of oily drops which sink to the bottom: the action is completed in 18 or 24 hours. — The oily liquid, after being washed and dried, begins to boil at  $90^\circ$ , but the greater part of it distils over between  $115^\circ$  and  $119^\circ$ . This portion, after being shaken up with oxide of lead and redistilled, boils at  $117^\circ$ , and exhibits by analysis the composition of monochloracetone. It is a colourless, very limpid liquid, which strongly irritates the nose and eyes, producing a copious flow of tears. Its sp. gr. is 1.14 at  $14^\circ$ . Vapour-density, 3.40.

					Riche.						
6 C	.....	36.0	...	38.22	.....	38.98	...	...	37.65	...	38.80
5 H	.....	5.0	...	5.40	.....	5.54	...	...	5.46	...	5.26
Cl	.....	35.5	...	38.92	.....	38.61					
2 O	.....	16.0	...	17.46							
<hr/>											
C <sup>6</sup> H <sup>5</sup> ClO <sup>2</sup>	.....	92.5	...	100.00							

		Vol.	Density.
C-vapour	.....	6	2.4960
H-gas	.....	5	0.3465
Cl-gas	.....	1	2.4543
O-gas	.....	1	1.1093
<hr/>			
Vapour of Monochloracetone	.....	2	6.4061
		1	3.2030

Monochloracetone is neutral to test-paper and is not altered, either by contact with the air or by distillation. It does not mix immediately with water, but appears to dissolve slowly in it: the solution thus formed does not precipitate nitrate of silver. — When kept in contact with boiling water for some hours, it disappears entirely and the liquid precipitates nitrate of silver; but on evaporating the water, nearly the whole of the liquid is deposited unaltered. — With potash in aqueous or alcoholic solution it forms brown products; ammonia in the state of gas or in aqueous or alcoholic solution, also solution of carbonate of ammonia, acts in the same manner, forming a deposit of sal-ammoniac. — Recently precipitated oxide of silver attacks it slightly at ordinary temperatures, but the action is not easily completed, even at  $100^{\circ}$ . The product is a brown liquid, soluble in ether and becoming glutinous when evaporated: it does not appear to contain either acetate or propionate of silver (A. Riche, *Compt. rend.* 49, 176).

*Monobromacetone.*  $C^6H^5BrO^2$ . — When a weak current of electricity is passed through a mixture of hydrobromic acid and acetone, hydrogen is evolved at the negative pole; but the bromine which would otherwise be eliminated at the positive pole acts upon the acetone, forming monobromacetone, which, in the course of 24 hours, is deposited in the form of an oil. This liquid, washed, dried, and distilled, begins to boil at about  $100^{\circ}$ , but the temperature rises quickly to  $140^{\circ}$ . A large quantity of liquid over between  $140^{\circ}$  and  $145^{\circ}$ ; but during the distillation, the liquid blackens and gives off hydrobromic acid. — This portion, freed from hydrobromic acid by a current of dry hydrogen and agitation with oxide of lead, exhibits a composition agreeing with the formula  $C^6H^5BrO^2$ . It is a colourless liquid, but turns brown after a few minutes. It irritates the eyes so strongly that the atmosphere of a room in which a few drops have been spilt becomes unendurable. (Riche, *Compt. rend.* 49, 178.)

A mixture of acetone and hydriodic acid behaves in a similar manner when an electric current is passed through it: iodine dissolves in the acetone, and an oil containing a considerable quantity of iodine falls to the bottom. This oil, after repeated washing, yields a few colourless needles, which are probably *moniodacetone*. (Riche.)

*Bichloracetone.*  $C^6H^4Cl^2O^2$ . — This compound was first obtained by Kane (who called it *mesitic chloral*) by passing dry chlorine-gas into anhydrous acetone. Fittig, who has recently prepared it by the same process, finds that, after washing with cold water and drying with chloride of calcium, the greater portion of the product distils between  $110^{\circ}$  and  $175^{\circ}$ , and by repeated rectification of this portion, an oil is obtained which distils constantly at  $120^{\circ}$ . — According to Städeler, this compound is most easily obtained by mixing acetone in a capacious flask with twice its volume of strong hydrochloric acid diluted with an equal bulk of water, and adding pulverised chlorate of potash by small portions. The liquid becomes strongly heated, the chlorine is completely absorbed, and bichloracetone quickly separates in the form of a heavy oily liquid.

Bichloracetone is an oily liquid of sp. gr. 1.236 at  $21^{\circ}$ . Boiling point  $121.5^{\circ}$  (Fittig);  $116.5^{\circ}$  (Städeler). Vapour-density 4.32. It is insoluble in water, but mixes in all proportions with alcohol and ether. (Fittig.)

				Fittig.	
6 C	.....	36	....	28.4	.....
4 H	.....	4	....	3.1	.....
2 Cl	.....	71	....	55.9	.....
2 O	.....	16	....	12.6	.....
<hr/>				<hr/>	
$C^6H^4Cl^2O^2$	.....	127	....	100.0	.....

		Vol.	Density.
C-vapour	.....	6	.....
H-gas	.....	4	.....
Cl-gas	.....	2	.....
O-gas	.....	1	.....
<hr/>		<hr/>	
Vapour	.....	2	.....
		1	.....

Schweizer's *xylic chloral* (ix, 44), obtained by the action of chlorine-gas on lignone, is probably also identical with bichloracetone.

Bichloracetone is not decomposed by alkalis in moderate quantity; but when treated with a considerable excess of alkali, it yields a chloride of the metal and a salt of an acid, which Kane called pteleic acid and supposed to contain  $C^6H^4O^4$ , but which is probably either acetic or monochloracetic acid. (Städeler.)

Bichloracetone unites with *alkaline bisulphites*, forming crystalline compounds. — When shaken up with a concentrated solution of *bisulphite of soda*, it forms a clear liquid, which, after some hours, deposits colourless nacreous laminæ, easily soluble in water, and having the unpleasant odour of bichloracetone. After being pressed between paper and dried over oil of vitriol, they gave by analysis 13.8 p. c. sulphur and 29.3 chlorine, corresponding to the formula  $C^6H^4Cl^2O^2 + NaO, 2SO^2 + 2Aq.$  (Fittig.)

*Terchloracetone*,  $C^6H^3Cl^3O^2$ , and *Tetrachloracetone*,  $C^6H^2Cl^4O^2$ . — Bouis (vii, 262) obtained these compounds by the action of chlorine on wood-spirit (probably containing acetone). The so-called *methylic choral*,  $C^{12}H^8Cl^5O^5$ , which Weidmann & Schweizer obtained by the action of chlorine on wood-spirit (vii, 261) was probably a hydrated mixture of bi- and ter-chloracetone:



It does not appear possible to form any of the higher chloracetones by the direct action of chlorine upon acetone, even in sunshine. (Fittig.) Some of these higher substitution-products are produced by the continued action of a mixture of hydrochloric acid and chlorate of potash upon acetone, but the action is accompanied with the evolution of dangerously explosive gases, and the products are very difficult to separate one from the other. (Städeler.)

*Pentachloracetone*.  $C^6HCl^5O^2$ . — This compound is produced by the action of hydrochloric acid and chlorate of potash on several organic compounds, viz., kinic acid, citric acid, gallic acid, pyrogallie acid, kinone, catechucic acid, muscular flesh, albumen, salicylic acid, indigo, and tyrosin; on the other hand, glycocol, leucin, tartaric acid, acetic acid and alcohol do not yield a trace of it.

**Preparation.** Chlorate of potash is added in considerable quantity to an aqueous solution of kinic acid, the liquid is heated to the boiling point, and strong hydrochloric acid added in such portions that chlorine and chlorous acid may be continually evolved. During this operation, explosions frequently take place which shatter the receiver, even though cooled with ice or snow; to avoid loss, therefore, the receiver should be frequently changed. — If the distillate contains any notable quantity of chlorokinone, it must be returned to the retort and redistilled. The distillates are partly concentrated by repeated rectification over chloride of calcium, and the portions of oil which separate in each distillation are collected together. If the oily product is tolerably free from other oily products which form at the same time, it solidifies in a white crystalline mass, when covered with water and exposed to a temperature of  $4^{\circ}$  to  $5^{\circ}$ . If no crystallization takes place at that temperature, the impure product must be shaken up with ice-cold water, and the clarified solution decanted and heated to about  $60^{\circ}$ , whereupon the greater portion of the dissolved oil separates out. This portion is collected, and the water is used for fresh extractions of the crude product. — The oil thus obtained is still impure, and generally has a rather strong yellow colour. To purify it, it is converted into the crystalline hydrate by covering it with water and exposing it to a low temperature, and the crystals are repeatedly pressed between paper to free them from a yellow oil which does not solidify.

To obtain the anhydrous compound, the crystals are heated in a test-tube till they melt; two liquids are thus formed, the upper of which is watery and the lower oily. The latter consists of pentachloracetone, which is to be removed with a pipette and dried over oil of vitriol in vacuo.

**Properties.** Colourless, rather mobile liquid, having a burning aromatic taste and a peculiar odour, like that of chloral. Sp. gr. between 1.6 and 1.7. It remains liquid at  $20^{\circ}$ , volatilises slowly in the air at ordinary temperatures, and boils at about  $190^{\circ}$ , apparently without decomposition. With vapour of water it distils easily and without alteration. It produces transient grease stains on paper, and is not turned brown by strong sulphuric acid.

					Städeler.
6 C	.....	36	....	15.62	..... 15.50
H	.....	1	....	0.43	..... 0.50
5 Cl	.....	177.5	....	77.01	..... 77.09
2 O	.....	16	....	6.94	..... 6.91
<hr/>					
$C^6HCl^5O^3$	.....	280.5	....	100.00	..... 100.00

The oily liquid which Plantamour obtained (xi, 441) by exposing citrate of soda to the action of chlorine in sunshine, and to which he assigned the formula  $C^6Cl^4O^3$ , was doubtless also pentachloracetone in an impure state. It had a density of 1.66 at  $15^{\circ}$ , boiled at  $190^{\circ}$ , and gave by analysis 15.99 p. c. carbon and 75.49 chlorine.

**Hydrate.**  $C^6HCl^5O^3 + 8HO$ . — Pentachloracetone shaken up with water and exposed to a temperature a little below  $0^{\circ}$ , is converted into a white crystalline hydrate which when dry looks very much like chlorate of potash. The crystals are sometimes  $\frac{1}{4}$  of an inch in diameter. They are rhombic tables of  $116^{\circ} 24'$  and  $63^{\circ} 36'$ , frequently also converted into hexagonal prisms by truncation of the acute angles. They

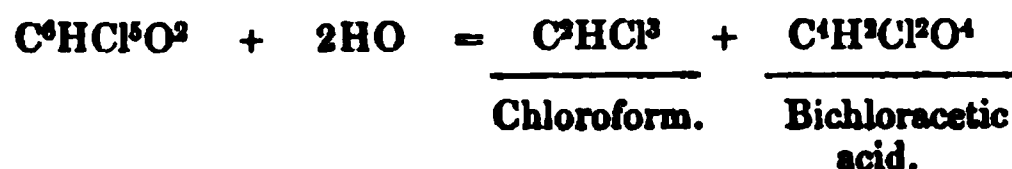
melt between  $16^{\circ}$  and  $17^{\circ}$  and volatilize slowly in the air at the same temperature. Heated in a glass tube, they are converted into a milky liquid, which at about  $50^{\circ}$  separates into two clear liquids, the upper of which is anhydrous pentachloroacetone.

					Städeler.
6 C	.....	36.0	....	11.90	..... 11.60
9 H	.....	9.0	....	2.98	..... 3.07
5 Cl	.....	177.5	....	58.68	..... 58.38
10 O	.....	80.0	....	26.44	..... 26.35
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$C^5HCl^5O^2 + 8Aq$	.....	302.5	....	100.00	..... 100.00

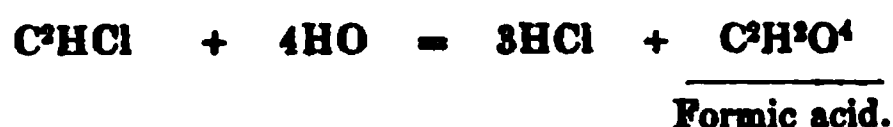
*Aqueous solution.* Water at  $0^{\circ}$  takes up  $\frac{1}{16}$  of its volume of anhydrous pentachloroacetone, and on the other hand, pentachloroacetone takes up a certain quantity of water without change of appearance; but it then becomes turbid at the heat of the hand, like hydrated conine.

The aqueous solution saturated at  $0^{\circ}$  likewise becomes milky at a gentle heat, and clear again at  $50^{\circ}$ , by separation of the pentachloroacetone — this separation is likewise effected by the addition of common salt, sal-ammoniac and other soluble salts.

The solution is distinctly acid, and may apparently be neutralised with baryta-water without alteration; but when the crystallized hydrate is triturated with baryta or lime, a distinct odour of chloroform is evolved. The solution nearly neutralised with baryta, remains perfectly clear on boiling, but if previously supersaturated with ammonia, it deposits carbonate of baryta. — The alcoholic solution of pentachloroacetone mixed with alcoholic solution of potash, deposits cubical crystals of chloride of potassium, mixed with scaly crystals of another salt, probably bichloroacetate of potash; the solution is found to contain formic acid :



and :



Plantamour, by treating with alcoholic potash the pentachloroacetone produced by the decomposition of citric acid (p. 466), likewise obtained, together with chloride of potassium, a scaly crystalline salt, to which he assigned the formula  $C^4Cl^2KO^4$ : it is most probable, however, that this salt was really bichloroacetate of potassium,  $C^4HCl^2KO^4$ , the formula of which differs from that given by Plantamour only by 1 At. H.

Pentachloroacetone dissolves in all proportions in *alcohol* and in *ether*. (Städeler.)

*Hexachloroacetone.*  $C^6Cl^6O^2$ . — This is the compound which Plantamour obtained (*loc. cit.*) by the action of chlorine gas in sunshine on an aqueous solution of citric acid. It is an oily liquid of peculiar pungent odour, sp. gr. 1.75 at  $10^{\circ}$ , and boiling between  $200^{\circ}$  and  $201^{\circ}$ . It makes transient grease-spots upon paper; gradually reddens litmus-paper; and, forms with water, at a temperature not above  $6^{\circ}$ , a crystalline hydrate,

2 H 2

$C^6Cl^6O^2 + 2Aq$ , which melts at a temperature above  $15^{\circ}$ , with separation of the oil.

					Plantamour.
6 C	.....	36	....	13.6	..... 13.5
6 Cl	.....	213	....	80.4	..... 79.8
2 O	.....	16	....	6.0	..... 6.7
<hr/>					
$C^6Cl^6O^2$	.....	265	....	100.0	..... 100.0

Plantamour assigned to this compound the formula  $C^6Cl^6O^2$ , and to the hydrate  $C^6Cl^6O^2 + 3Aq$ .

Page 8.

*Action of Nitric Acid upon Acetone.* — Fittig, by adding acetone in successive small portions to fuming nitric acid in a flask externally cooled, and diluting with water as soon as the first action is over, obtained a yellow, viscid, explosive oil, containing 38.3 p. c. carbon and 2.8 hydrogen, and exhibiting the characters of a nitro-compound. It is decomposed by sulphydric acid and sulphide of ammonium, with separation of sulphur; but the products are brown tarry liquids which show no tendency either to crystallize or to unite with acids.

Page 9.

*Action of Pentachloride of Phosphorus on Acetone.* — Pentachloride of phosphorus forms with acetone, two compounds, viz., *methylchloracetol*  $C^6H^6Cl^2$ , boiling at  $70^{\circ}$  and *chloropropylene*,  $C^6H^5Cl$ , boiling at about  $30^{\circ}$ . — Methylchloracetol treated with silver-salts, ammonia, ethylate of sodium, or alcoholic potash, is resolved into  $C^6H^5Cl$  and hydrochloric acid. — The other body,  $C^6H^5Cl$ , unites with bromine and forms the compound  $C^6H^5Cl.Br^2$ , which, by fractional distillation, is obtained in the form of a very heavy liquid having a saccharine taste. Its sp. gr. at  $0^{\circ}$  is 2.064; vapour density 8.22; boiling point  $170^{\circ}$ .

					Friedel.
6 C	.....	36.0	.....	15.22	..... 15.06
5 H	.....	5.0	.....	2.11	..... 2.17
Cl	.....	35.5	.....	15.02	..... 15.95
2 Br	.....	160.0	.....	67.65	..... 68.13
<hr/>					
$C^6H^5Cl.Br^2$	.....	236.5	.....	100.00	..... 99.99

		Vol.	Density.
C-vapour	.....	6	..... 2.4960
H-gas	.....	5	..... 0.3465
Cl-gas	.....	1	..... 2.4543
Br-vapour	.....	2	..... 11.0930
<hr/>			
Vap. of $C^6H^5Cl.Br^2$	.....	2	..... 16.3898
		1	..... 8.1949



This chlorobromide treated with alcoholic potash yields another chlorobromide,  $C^6H^4ClBr$ , which boils at  $105^\circ$ , and gives by analysis 23.47 p. c. carbon and 2.85 hydrogen (calculation: 22.82 C and 2.58 H). The same body is produced by treating  $C^6H^5ClBr^2$  with silver-salts.

Methylchloracetol is isomeric, but not identical with bichloride of propylene  $C^3H^2Cl^2$ , which boils, according to Friedel, between  $93^\circ$  and  $98^\circ$ . But the compound  $C^6H^5Cl$  obtained from methylchloracetol is identical with chloropropylene obtained from chloride of propylene. Chloropropylene prepared from chloride of propylene, yielded, when passed into bromine, a chlorobromide which boiled at  $170^\circ$ , like that derived from acetone. Its composition, as determined by analysis (13.91 p. c. C, 1.99 H, 17.01 Cl and 66.76 Br) did not however agree very closely with the formula  $C^6H^5ClBr^2$ , probably in consequence of an admixture of chloride of bromopropylene  $C^6H^5BrCl^2$ .

The preceding facts show that acetone is related to the propylene series. (Friedel, *Bull. Soc. Chim. de Paris*, i, 26; *Ann. Pharm.* xii, 236.

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Page 10.

For the action of *ammonia* on acetone see page 378 of this volume.

*Acetone with Bisulphite of Ammonia.* — When an alcoholic solution of bisulphite of ammonia is mixed with acetone till permanent turbidity is produced, the liquid becomes hot, and after a few seconds deposits laminæ resembling cholesterin, which quickly aggregate into a heavy crystalline powder. It is soluble in water and alcohol, insoluble in ether. It decomposes rather easily, even at ordinary temperatures, and smells of ammonia and sulphurous acid. (Städeler.)

				Städeler.
$NH^3$	.....	17	.... 10.83	..... 10.99
$SO^2$	.....	64	.... 40.77	..... 40.13
2 HO	.....	18	.... 11.46	
$C^6H^6O^2$	.....	58	.... 36.94	
<hr/>				
$C^6H^6O^2 + (NH^4O, HO, 2SO^2)$		157	.... 100.00	

The formula is equivalent to that of *cystin* + 4HO, but the compound is not converted into cystin by heat. (Städeler.)

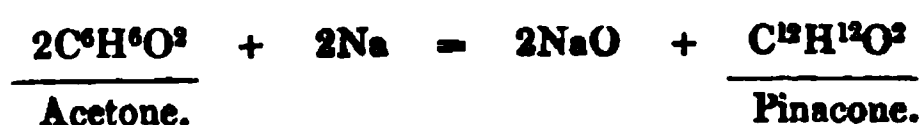
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Page 15.

*Action of Sodium on Acetone. — Pinacone.*  $C^{12}H^{12}O^2$ . — Sodium is violently attacked by anhydrous acetone, but without evolution of hydrogen, and hydrate of soda is separated in white flakes. The liquid gradually assumes a pasty consistence, and the sodium becomes coated with oxide, so that it no longer acts perceptibly on the acetone. On



subjecting the pasty mass to distillation, undecomposed acetone passes over first, and on increasing the heat, two liquids collect in the receiver, viz., a colourless watery layer, covered with a yellowish oil having an odour of peppermint. On pouring the distillate into a basin, so that the still remaining acetone may gradually evaporate, the watery liquid solidifies in a white crystalline mass, from which the oil may be separated by decantation and pressing between paper. The crystalline compound, which consists of *hydrate of pinacone*, may be further purified by two recrystallizations from a small quantity of hot water, the solutions being filtered through moistened paper to separate the last traces of oil. (Städeler.) The formation of pinacone may be represented by the equation :



and the anhydrous pinacone thus produced appears to take water from another portion of the acetone, converting it into *phorone* (p. 342) which is the oily liquid formed at the same time :



The crystals of hydrated pinacone contain 14 At. water. According to the concentration of the aqueous solution and the quicker or slower rate of cooling, the compound separates, either in colourless four-sided tables very much like oxalate of methyl, or in long thin prismatic crystals; in both these forms it contains the same quantity of water. The crystals are very brittle, dissolve readily in water, and still more readily in alcohol, ether and acetone. They have no perceptible odour, and a somewhat faint and cooling taste. Near 42°, they melt to a clear homogeneous liquid, which begins to boil and give off water at 100°, the boiling point gradually rising as the water goes off. By performing the experiment in a narrow glass tube and gradually raising the temperature to 140°, a viscid liquid is at length obtained, which burns with a bright flame and appears to be anhydrous pinacone. It could not, however, be obtained in sufficient quantity for analysis; when 4 or 5 grms. were treated as above, a considerable quantity volatilized, and the residue still crystallized on cooling, even after the heating had been continued for several hours. Anhydrous pinacone is quickly converted into the hydrate on exposure to the air, and instantly when mixed with water.

<i>Hydrated Pinacone.</i>			<i>Städeler.</i>		<i>Fittig.</i>		
			<i>a.</i>	<i>b.</i>			
12 C .....	72 ....	31·86 ... ..	31·60 ....	31·63 .....	32·2 ....	32·4 ....	33·1
26 H .....	26 ....	11·50 .... ..	11·56 ....	11·52 .....	11·5 ....	11·6 ....	11·5
16 O .....	128 ....	56·64 .....	56·84 ....	56·85 .....	56·3 ....	56·0 ....	55·4
$\text{C}^{12}\text{H}^{12}\text{O}^2 + 14\text{Aq}$	226 ....	100·00 .....	100·00 ....	100·00 .....	100·0 ....	100·0 ....	100·0

Städeler's analysis *a* was made with the prismatic, *b* with the tabular crystals. Fittig regards the crystals as a *hydrate of paracetone*,  $\text{C}^6\text{H}^6\text{O}^2 + 6\text{Aq}$ , which, however, requires 32·1 p. c. carbon and only 10·7 hydrogen, a difference scarcely to be accounted for in the analysis of a well-defined crystalline compound: moreover, Städeler's view of their composition is more in accordance with the mode of formation, viz., by the de-oxydising action of sodium on acetone.

Anhydrous pinacone is metameric with *caproic aldehyde*,  $\text{C}^{12}\text{H}^{11}\text{O}^2, \text{H}$ , also with Williamson's *valyl-methyl*,  $\text{C}^{10}\text{H}^9\text{O}^2, \text{C}^2\text{H}^3$  (*Chem. Soc. Qu. J.* 4, 239), and Friedel's *butyryl-ethyl*,  $\text{C}^8\text{H}^7\text{O}^2, \text{C}^4\text{H}^6$  (*Ann. Pharm.* 108, 122).

By leaving the crystals of the 14-atom hydrate over oil of vitriol for a week and recrystallizing from anhydrous ether, Fittig obtained crystals of pinacone containing 4 At. water; and after three weeks standing over oil of vitriol, crystals were obtained whose composition was nearly that of pinacone with 2 At. water.

With 4 At. water.					Fittig.
12 C	.....	72	...	52.94	..... 53.3
16 H	.....	16	...	11.77	..... 11.8
6 O	.....	48	...	35.29	..... 34.9
<hr/>					
$C^{12}H^{12}O^2 + 4Aq$	...	136	...	100.00	..... 100.0

With 2 At. water.					Fittig.
12 C	.....	72	...	61.02	..... 60.8
14 H	.....	14	...	11.86	..... 11.5
4 O	.....	32	...	27.12	..... 27.7
<hr/>					
$C^{12}H^{12}O^2 + 2Aq$	...	118	...	100.00	..... 100.0

Lastly, by heating a solution of ammonia in acetone to 100° in sealed tubes, Fittig sometimes obtained crystals resembling the last, and giving by analysis 61.8 p. c. carbon and 10.8 hydrogen. Fittig regards these crystals as *paracetone*  $C^6H^6O^2$  (calc. 62.1 p. c. C and 10.3 H). The numbers do not however differ greatly from those deduced from the formula  $C^{12}H^{12}O^2 + 2Aq$ . Moreover, the analysis was made with only 0.115 grm. of substance and the crystals were not always obtained. Städeler suggests that the acetone from which they were produced might have been previously used in the preparation of pinacone—that is to say, recovered by distillation after treatment with sodium; and in that case would probably contain a small portion of pinacone. Städeler never obtained such crystals by heating acetone with ammonia, but only the syrupy compound described at page 10, vol. ix, which by spontaneous decomposition yields acetone.

The crystals of hydrated pinacone dissolve in concentrated sulphuric acid, with spontaneous rise of temperature, yellow colouring and gradual turbidity; on heating the solution, it assumes a deep brown-red colour, and the pinacone is gradually decomposed. — With strong potash-ley it may be heated without undergoing decomposition, merely melting into oily drops which do not mix with the potash-ley, but crystallize again on cooling. (Städeler.)

*Action of Quick Lime on Acetone.* — When well burnt marble is left, together with a quantity of acetone just sufficient to cover it, in a closed vessel for a considerable time (2 to 6 weeks), and the liquid then distilled without addition of water, two products are obtained, the one boiling below 150° the other above 200°.

By submitting the former to repeated fractional distillation, nearly half of it may be brought to the constant boiling point 129°, and the liquid thus obtained exhibits the composition and properties of *oxide of mesityl* (ix, 25). It is a transparent colourless oil, having a burning taste and an odour like that of peppermint, and burning with a bright flame. It is insoluble in water, but mixes in all proportions with alcohol and

ether. Sp. gr. 0·848 at 23°. Vapour density 3·67. Boiling point 131°. (Fittig.) According to Kane it boils at 120°.

				Fittig.	Kane.
12 C .....	72	...	73·4	73·15	73·16
10 H .....	10	...	10·2	10·35	10·55
2 O .....	16	...	16·4	16·50	16·29
$C^{12}H^{10}O^2$ .....	98	...	100·0	100·00	100·00

	Vol.	Density.
C-vapour .....	12	4·9920
H-gas .....	10	0·6930
O-gas .....	1	1·1093
Vap. of $C^{12}H^{10}O^2$ .....	2	6·7943
	1	3·3971

By nitric acid or by a mixture of nitric and sulphuric acid, oxide of mesityl is converted, with great evolution of heat, into a brown, tough, resinous mass, which is insoluble in water, but easily soluble in alcohol, and separates from the solution on evaporation still as a brown resinous mass. — Chlorine acts strongly on oxide of mesityl, forming a colourless oil which is heavier than water, and is decomposed by distillation. It was therefore merely washed with water and placed under a bell-jar near sticks of potash. It then gave by analysis 45·4 p. c. chlorine: whence it may have been impure *bichloromesitic ether*,  $C^{12}H^2Cl^2O^2$ , the formation of which requires 42·5 p. c. Cl. (Fittig.)

Oxide of mesityl does not unite with alkaline bisulphites, and is thereby distinguished from *dumasin*, which is isomeric with it.

The portion of the original distillate which boiled above 200°, was partially decomposed by fractional distillation; nevertheless two portions were obtained, one distilling between 210° and 220°, the other between 220° and 230°, both of which exhibited very nearly the composition of *phorone*,  $C^{18}H^{14}O^2$ .

				Fittig.	
				210° to 220°	220° to 230°
18 C .....	108	...	78·3	77·6	78·0
14 H .....	14	...	10·2	10·2	9·8
2 O .....	16	...	11·5	12·2	12·2
$C^{18}H^{14}O^2$ .....	138	...	100·0	100·0	100·0

According to Völckel (ix, 16), the product of the action of quick lime on acetone is *xylite-oil*,  $C^{12}H^9O$  (or rather  $C^{24}H^{18}O^3$ ), which however requires 80·9 p. c. carbon, a quantity which differs considerably from the analytical result.

The following table exhibits a list of the bodies, arranged according to their boiling points, which are produced by the action of strong sulphuric acid or of caustic alkalis on acetone; they are all produced by the abstraction of water from two or more molecules of acetone.

		Boiling point.
Xylitic naphtha	$C^{24}H^{22}O^6 = 4C^6H^6O^2 - 2HO$	110° to 120° (Völckel)
Oxide of mesityl	$C^{12}H^{10}O^2 = 2C^6H^6O^2 - 2HO$	131° (Fittig, Kane)
Mesitylene	$C^{18}H^{12} = 3C^6H^6O^2 - 6HO$	155° to 160° (Hofmann)
Phorone (?)	$C^{18}H^{14}O^2 = 3C^6H^6O^2 - 4HO$	210° to 220° (Fittig)
Xylite-oil	$C^{24}H^{18}O^3 = 4C^6H^6O^2 - 6HO$	above 200° (Löwig, Weidmann)

**Methyl-acetone, Ethyl-acetone, and Dumasin.**R. FITTIG. *Ann. Pharm.* 110, 18.

When the oily liquid which is obtained, together with acetone, by the dry distillation of acetates, and floats on the top of the crude acetone, is subjected to fractional distillation, after being dehydrated by chloride of calcium, pure acetone passes over below  $60^{\circ}$ , and the liquid which distils between  $60^{\circ}$  and  $130^{\circ}$ , may be resolved almost completely, by repeated fractional distillation, into three compounds, viz., methyl-acetone, ethyl-acetone, and dumasin.

*Methyl-acetone*,  $C^5H^8O^2 = C^5H^6(C^2H^2)O^2$ , is a colourless liquid which smells like acetone and mixes in all proportions with water and alcohol. Sp. gr. 0.838 at  $19^{\circ}$ . Boils between  $75^{\circ}$  and  $77^{\circ}$ .

				Fittig.
8 C .....	48	....	66.6	..... 66.0
8 H .....	8	....	11.1	..... 11.2
2 O .....	16	....	22.3	..... 22.8
<hr/>				
$C^5H^8O^2$ .....	72	....	100.0	..... 100.0

Methylacetone forms with *bisulphite of soda*, a crystalline compound containing  $C^5H^8O^2 + (NaO, HO, 2SO^2) + Aq$  or  $C^5H^7NaS^2O^6 + 3Aq$ . It is very soluble in water and cannot be purified by recrystallization. As it contained an excess of bisulphite of soda, which could not be removed, the sodium and sulphurous acid were first determined and found to be Na = 15.3 p. c. and  $S^2O^4 = 41.6$  p. c. The sum of these, viz., 56.9, was then deducted from 100, and the remainder = 43.1 considered as the sum of the carbon, hydrogen and oxygen =  $C^5H^7O^2 + 3Aq = C^5H^{10}O^2$ . The quantities of carbon, hydrogen and oxygen calculated from this formula are 21.1 C + 4.4 H + 17.6 O = 43.1, and with these the quantities of carbon and hydrogen found by burning the salt with chromate of lead agreed very nearly, viz., 20.4 C and 4.5 H. (Fittig.)

*Ethyl-acetone*.  $C^{10}H^{10}O^2 = C^5H^5(C^5H^5)O^2$ . — Transparent colourless liquid, smelling faintly of acetone, sparingly soluble in water, but miscible in all proportions with alcohol. Sp. gr. 0.842 at  $19^{\circ}$ . Boiling point between  $90^{\circ}$  and  $95^{\circ}$ .

				Fittig.
10 C .....	60	....	69.8	..... 70.4
10 H .....	10	....	11.6	..... 11.2
2 O .....	16	....	18.6	..... 18.4
<hr/>				
$C^{10}H^{10}O^2$ .....	86	....	100.0	..... 100.0

With *bisulphite of soda*, ethyl-acetone forms the compound  $C^{10}H^{10}O^2 + (NaO, HO, 2SO^2) + Aq$  or  $C^{10}H^9NaS^2O^6 + 3Aq$ , which crystallizes as colourless shining nacreous laminae, very soluble in water. They were purified for analysis by pressure between paper and drying over sulphuric acid, but as they contained excess of bisulphite of soda, the analysis was made as in the preceding case. The sulphurous acid and sodium

were found to be together 46.6 p. c.; and this deducted from 100 leaves 53.4 for the weight of the  $C^{10}H^{10}O^3 + 3Aq$  or  $C^{10}H^{12}O^5$  in 100 parts of the salt.

Calculation.				Fittig.	
10 C .....	60	...	28.6	.....	29.0
12 H .....	12	...	5.7	.....	6.3
5 O .....	40	...	19.1		
<hr/>					
	112	...	53.4		

*Dumasin.*  $C^{12}H^{10}O^3$ . — Properties (ix, 25). — According to Fittig it boils between 120° and 125°.

				Fittig.	
12 C .....	72	...	73.5	.....	73.7
10 H .....	10	...	10.2	.....	11.1
2 O .....	16	...	16.3	.....	15.2
<hr/>					
$C^{12}H^{10}O^3$ .....	98	...	100.0	.....	100.0

Isomeric with oxide of mesityl, from which however it is distinguished by combining with alkaline bisulphites.

Strong nitric acid converts dumasin into oxalic acid; dilute nitric acid exerts scarcely any action upon it.

When dumasin is shaken up or left to stand for some time in contact with a concentrated solution of *bisulphite of soda*, the oil which floats on the surface solidifies completely to a crystalline mass resembling the preceding compound and of similar constitution. It dissolves readily in water, but boiling water decomposes it immediately, and separates the dumasin. Its instability and the impossibility of completely separating the excess of bisulphite of soda, rendered it difficult to obtain satisfactory analyses. The quantity of sulphur found varied from 16.2 to 19.3; the carbon from 26.8 to 30.8 and the hydrogen from 5.6 to 6.1 per cent. Hence the compound appears to be  $C^{12}H^8NaS^2O^6 + 6Aq$ , which requires 30.2 p. c. C 6.3 H and 13.4 S.

*Bichlorodumasin.*  $C^{12}H^8Cl^2O^3$ . — Obtained by distilling dumasin with hydrochloric acid and peroxide of manganese. It is a colourless oil, heavier than water, boiling between 150° and 155°, and not capable of combining with alkaline bisulphites.

				Fittig.	
12 C .....	72	...	43.1	.....	43.2
8 H .....	8	...	4.8	.....	5.4
2 Cl .....	71	...	42.5	.....	41.7
2 O .....	16	...	9.6	.....	9.7
<hr/>					
$C^{12}H^8Cl^2O^3$ .....	167	...	100.0	.....	100.0

Page 37.

**Acetonic Acid.  $C^3H^3O^4$ .**

Produced by the action of hydrochloric and hydrocyanic acid upon acetone :



The mode of formation is analogous to that of mandelic acid from bitter almond oil. — To prepare the acid, acetone is mixed with aqueous hydrocyanic and hydrochloric acid, and the mixture, after having stood for some time, is boiled, and afterwards evaporated over the water-bath. The brownish syrupy residue solidifies on cooling, and may be almost wholly freed by pressure between paper, from a brown very bitter substance, which adheres to it. The pressed mass consists almost entirely of sal-ammoniac and acetic acid, and the latter may be dissolved out by ether, and purified by recrystallization from water and from ether. (Städeler, *Ann. Pharm.* 111, 320.)

Acetic acid is odourless, has a strongly acid taste, and reddens litmus. It is easily dissolved by water, alcohol, and ether, and crystallizes from the solutions in small colourless prisms, generally arranged in crosses. It volatilizes to a certain extent with vapour of water.

				Städeler.
8 C .....	48	...	46.15	46.00
8 H .....	8	...	7.70	7.68
6 O .....	48	...	46.15	46.32
<hr/>				
$C^3H^3O^4$ .....	104	...	100.00	100.00

Homologous with lactic acid  $C^3H^5O^4$ , from which it differs by  $C^2H^2$ .

Heated in a glass tube, it melts into a colourless oily liquid, which mounts up the sides of the tube without actually subliming. The drops solidify quickly on cooling, and appear to consist of unaltered acetic acid. — Heated with hydrate of potash, it gives off the odour of acetone. — It is not altered by oil of vitriol in the cold, but on heating the mixture, it turns brown and gives off a large quantity of gas. — A moderately dilute solution of the acid neutralized with ammonia is not precipitated by nitrate of silver; but the mixture gradually deposits metallic silver in dark flocks.

*Barium-salt*,  $C^3H^3BaO^4$ . — Obtained by neutralizing the acid with baryta-water and evaporating to a syrup. By slow cooling, it is obtained in small thin prisms, apparently with rhombic base, which gradually change to a crystalline magma. By rapid cooling, the syrupy solution solidifies to a satiny, long-fibred, crystalline mass. After drying at  $110^\circ$ , or in vacuo, it does not diminish sensibly in weight at  $180^\circ$ . At a stronger heat, it decomposes and gives off vapours smelling like burnt tartar, but also pungent like acetone. Gave by analysis, 43.4 and 42.7 p. c. baryta, the formula requiring 44.6 p. c. The difference arises from

impurity, as the salt could not be purified by recrystallization, on account of its great solubility.

*Zinc-salt.*  $C^8H^7ZnO^6 + 2 Aq.$ — Obtained by boiling the aqueous acid with carbonate of zinc, filtering the boiling solution, and exhausting the residue with boiling water. The solution on cooling, deposits the salt in thin, colourless, microscopic, six-sided tables or prisms, exactly like those of lactate of zinc. It is sparingly soluble in water, insoluble in alcohol and ether. When heated, it decomposes without melting, giving off vapours which smell like those emitted by the barium-salt.

	<i>Air-dried.</i>				<i>Städeler.</i>
ZnO .....	40.5	.....	26.39	.....	26.67
$C^8H^7O^6$ .....	95.0	.....	61.88	.....	
2 HO .....	18.0	.....	11.73	.....	11.27
<hr/>					
$C^8H^7ZnO^6 + 2Aq$ .....	153.5	.....	100.00	.....	

The amount of water is the same as that of sarcoholactate of zinc  $C^8H^5ZnO^6 + 2Aq$  (xi, 500).

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Page 38.

### Acetal.

Acetal is isomeric but not identical (as stated at page 521, vol. xii), with biethyl-glycol,  $C^4H^4(C^2H^5)^2O^2$ ; the latter boils at  $123.5^\circ$ , whereas acetal boils at  $104^\circ$  to  $106^\circ$  (see page 427, of this volume).

For the transformation of acetal into aldehyde and *vice versa* (see page 437).

*Action of Pentachloride of Phosphorus on Acetal.*— Pentachloride of phosphorus acts violently on acetal, forming chloride of ethyl and oxychloride of phosphorus, but no chloride of ethylidene or chloride of vinyl. — When 2 At.  $PCl^5$ , are made to act on 1 At. acetal, and the product is treated with water, an oil separates which appears to have the composition  $C^8H^9Cl^3$ . — But when 1 At.  $PCl^5$ , is added to 1 At. acetal, the mixture being well cooled, and the product decomposed by adding small pieces of ice, another chlorine-compound is formed, probably  $C^8H^9ClO^2$ , the same indeed, as Wurtz and Frapollé obtained by the action of hydrochloric acid on a mixture of aldehyde and absolute alcohol. — The two reactions may perhaps take place as follows :





The two compounds are very unstable, and were not obtained in sufficient quantity for exact analysis.

If the preceding formulæ and reactions are correct, the constitution of acetal may be represented by the formula  $\begin{matrix} \text{C}^3\text{H}^3\text{O}^3 \\ \text{C}^4\text{H}^5 \end{matrix} \left. \vphantom{\begin{matrix} \text{C}^3\text{H}^3\text{O}^3 \\ \text{C}^4\text{H}^5 \end{matrix}} \right\} \text{O}^2$ , that is to say, alcohol, in which 1 At. H is replaced by the radical  $\text{C}^3\text{H}^3\text{O}^3$ . This radical would form the chloride  $\text{C}^3\text{H}^3\text{O}^3\text{Cl}$ , and the perchloride  $\text{C}^3\text{H}^3\text{Cl}^3$ ; but being rather unstable, it may easily resolve itself into aldehyde and ethyl,  $\text{C}^3\text{H}^3\text{O}^3 = \text{C}^4\text{H}^4\text{O}^2 + \text{C}^4\text{H}^5$ ; and in fact, acetal treated with acetic acid or acetic anhydride (p. 437), does yield aldehyde and acetate of ethyl. (Beilstein, *Bull. Soc. Chim. de Par.* 46; *Ann. Pharm.* 112, 240.)

### Chloracetals.

A. LIEBEN. *N. Ann. Chim. Phys.* 52, 313.

These compounds are formed, together with acetal, aldehyde, formiate of ethyl, and acetate of ethyl, by the action of chlorine on hydrated alcohol, the relative quantities of the several substitution-compounds varying according to the strength of the alcohol.

When chlorine is passed into alcohol of ordinary strength (80 per cent.), and the heavy oil which separates on addition of water, is washed several times with aqueous chloride of calcium, then dehydrated, and submitted to fractional distillation, it begins to boil at  $80^\circ$ , and the boiling point gradually rises to about  $200^\circ$ , not however, remaining stationary at any intermediate point. The portion which distils below  $120^\circ$ , consists of aldehyde and compound ethers; that which distils above  $120^\circ$ , which is in larger quantity than the former, contains monochloracetal and bichloracetal. On submitting this portion to fractional distillation, the greater part passed over between  $170^\circ$  and  $185^\circ$ ; this consisted chiefly of *bichloracetal*, which may be obtained nearly pure by again subjecting this same portion to fractional distillation. To separate the *monochloracetal*, the portion of the second distillate boiling below  $170^\circ$ , and the portions of the first distillate which passed over below  $120^\circ$ , were heated for several days with solution of potash, whereby a considerable quantity of chloride of potassium was formed, together with a yellow oily liquid, which floated on the aqueous solution. The watery liquid contained formic acid. The oil being distilled fractionally, a considerable portion passed over between  $156^\circ$  and  $165^\circ$ , and the boiling point of the remainder rose to  $180^\circ$ . This latter portion contained bichloracetal. The former portion did not yield a liquid of perfectly stable boiling point, but a considerable portion consisting, chiefly of monochloracetal, passed over between  $154^\circ$  and  $159^\circ$ .

*Monochloracetal*,  $\text{C}^{12}\text{H}^{12}\text{ClO}^4$ , is a colourless liquid, having an ethereal, aromatic odour, and boiling at about  $155^\circ$ . Vapour-density, 5.38. It is perfectly neutral, insoluble in water, soluble in alcohol, not attacked by



potash-ley. It does not precipitate nitrate of silver, either in the cold when heated.

Between 154° and 159°.				Lieben.
12 C	.....	72.0	... 47.21	..... 46.70
13 H	.....	13.0	... 8.52	..... 8.48
Cl	.....	35.5	... 23.28	..... 24.73
4 O	.....	32.0	... 20.99	..... 20.09
$C^{12}H^{13}ClO^4$	.....	152.5	... 100.00	..... 100.00

	Vol.	Density.
C-vapour	12	4.9920
H-gas	13	0.9009
Cl-gas	1	2.4543
O-gas	2	2.2186
Vapour	2	10.5658
	1	5.2829

A product collected between 158° and 165° gave 45.52 p. c. C and 8.24 H ; another collected at 160° gave 46.00 C and 8.55 H. These products evidently contained more bichloracetal than the portion collected between 154° and 159°.

*Bichloracetal.*  $C^{12}H^{13}Cl^2O^4$ . — Obtained by rectifying the portions of the second distillate (p. 477), which boiled between 170° and 185°, and collecting apart that which passed over at 180°.

Colourless neutral liquid, having an ethereal aromatic odour. Sp. gr. 1.1383 at 14. Boils at about 180°. Vapour-density 6.45.

				Lieben.		
12 C	.....	72	... 38.50	..... 39.1	... 38.26	... 38.41
12 H	.....	12	... 6.42	..... 6.66	... 6.62	... 6.23
2 Cl	.....	71	... 37.97	..... 37.93		
4 O	.....	32	... 17.11	.....		
$C^{12}H^{13}Cl^2O^4$	.....	187	... 100.00			

	Vol.	Density.
C-vapour	12	4.9920
H-gas	12	0.8316
Cl-gas	2	4.9086
O-gas	2	2.2186
Vapour of Bichloracetal	2	12.9508
	1	6.4254

The product of the action of chlorine upon alcohol of ordinary strength, does not appear to contain acetal, and is certainly free from Dutch liquid, which has sometimes been supposed to form part of it. (Lieben.)

*Terchloracetal.*  $C^{12}H^{11}Cl^3O^4$ . — This compound is formed, together with bichloracetal, by the action of chlorine on highly concentrated (but not quite absolute) alcohol. Dumas gives the following analysis of a

portion of liquid thus obtained, the boiling point of which however is not stated.

					Dumas.
12 C	.....	72.0	...	32.50	..... 32.5
11 H	.....	11.0	...	4.96	..... 5.1
3 Cl	.....	106.5	...	48.08	..... 47.3
4 O	.....	32.0	...	14.46	..... 15.1
<hr/>					
C <sup>12</sup> H <sup>11</sup> Cl <sup>35.5</sup> O <sup>4</sup>	.....	221.5	...	100.00	..... 100.0

This liquid was evidently terchloracetal. Two other portions of liquid similarly obtained, the one boiling at 183°, and having a vapour-density of 6.7, and the other at 186°, with vapour-density 6.6, appear to be mixtures of bichloracetal and terchloracetal. [The calculated vapour-density of bichloracetal is 6.43, that of terchloracetal 7.67.] Another product analysed by Lieben, also boiling at 186°, exhibits a similar composition.

	Dumas.			Lieben.
	at 183°.	at 186°.		
Carbon.....	35.4	...	35.6	..... 36.72
Hydrogen.....	5.9	...	5.8	..... 6.36
Chlorine.....	45.1	...	44.2	
Oxygen.....	13.6	...	14.4	
<hr/>				
	100.0	...	100.0	

When chlorine is passed into very dilute alcohol (of 44 per cent.), kept in a state of ebullition till the chlorine is no longer absorbed, and the product is subsequently distilled, the distillate contains aldehyde, formate of ethyl, acetate of ethyl, acetal and monochloracetal; and the acid residue contains hydrochloric acid, together with a non-volatile acid, probably glycolic acid. — If the alcohol is kept cool, the chief products are aldehyde and acetal. (Lieben.)

Page 56.

## Ethylamine.

*Formation.* According to E. Meyer (*J. pr. Chem.* 68, 279), ethylamine is best prepared by the action of ammonia on iodide of ethyl. Wurtz's method of decomposing cyanate of ethyl with potash, also yields a good product. Strecker's process of decomposing sulphethamate of ammonia, is less productive. — Meyer finds also that ethylamine is formed during the preparation of cyanate of ethyl by distilling a mixture of ferrocyanide and sulphovinate of potassium, with addition of peroxide of manganese or oxide of copper. — *Cyanide of ethyl*, whether prepared by distilling sulphovinate of potassium with commercial ferrocyanide, or with pure cyanide of potassium, disappears when left in contact for some time with hydrochloric or sulphuric acid; and on distilling the solution, propionic acid is given off, and a salt of ammonia is left, together with a salt of ethylamine. This formation of ethylamine from cyanide of ethyl, is similar to that of ammonia from cyanide of hydrogen (vii, 401). — For the formation of ethylamine in the decomposition of cyanide of ethyl and silver (see page 458).

Ethylamine is formed when cyanate of potash is heated with sulphovinate of lime and hydrate of lime, and in larger quantity by heating a mixture of urea, caustic lime, and sulphovinate of lime. The urea is mixed with excess of quick lime; a quantity of sulphovinate of lime is added, equal to one-fifth of the weight of the urea; and the mixture is heated in a retort connected with a receiver containing hydrochloric acid. By evaporating the contents of the receiver to dryness, and treating the residue with a mixture of alcohol and ether to separate sal-ammoniac, a deliquescent chloride is obtained, which gives off ethylamine when heated with an alkali. — To obtain a good product, the salts must be well dried; sulphovinate of lime yields a larger quantity than sulphovinate of potash. (D. K. Tuttle, *Ann. Pharm.* 101, 288.)

A solution of ethylamine in absolute alcohol does not precipitate an alcoholic solution of iodine. — Iodide of nitrogen dissolves readily in ethylamine, forming a solution which becomes turbid when diluted with water, but clear and colourless on addition of a large quantity of water. The clear liquid yields, by evaporation, very hygroscopic crystals coloured yellow by free iodine. — No homologue of iodide of nitrogen appears to be formed. (Gilm. *Wien. Akad. Ber.* xx, 30, 126.)

*Separation of Ethylamine from Ammonia.* — This separation may be effected by treating the mixed bases with excess of tartaric acid, and digesting the evaporated residue with alcohol, which dissolves the bitartrate of ethylamine and leaves bitartrate of ammonia. (Meyer, *J. pr. Chem.* 67, 147.)

According to Meyer, ethylamine may be used (as originally suggested by Wurtz) for separating alumina from sesquioxide of iron, the alumina dissolving in the ethylamine, and the ferric oxide remaining undissolved. A mixture of 0.215 grm.  $\text{Al}_2\text{O}_3$  and 0.740 grm.  $\text{Fe}_2\text{O}_3$ , yielded, after separation in this manner, 0.214  $\text{Al}_2\text{O}_3$ , and 0.740  $\text{Fe}_2\text{O}_3$ .

*Sulphate of Ethylamine.* — This salt decomposes when boiled and gives off ethylamine. It forms with *sulphate of magnesia*, a double salt which crystallizes in transparent prisms containing 6 or 7 atoms of water. Analysis gave 8.96 p. c. magnesia, and 36.52 sulphuric acid ( $\text{SO}_3$ ); while the formula  $\text{MgO}, (\text{C}_2\text{H}_5\text{N}, \text{HO}), \text{S}^2\text{O}_6 + 7 \text{Aq.}$  requires 9.2  $\text{MgO}$ , and 36.88  $\text{SO}_3$ , and  $\text{MgO}, (\text{C}_2\text{H}_5\text{N}, \text{HO}), \text{S}^2\text{O}_6 + 6 \text{Aq.}$  requires 9.62  $\text{MgO}$ , and 38.46  $\text{SO}_3$ . It is difficult to dry the crystals completely between paper, and at  $100^\circ$ , ethylamine may be driven off as well as water. The crystals left over oil of vitriol for six weeks, lost 19.31 p. c. water, or about 4 At. (Meyer.)

Sulphate of ethylamine likewise forms crystallizable double salts with sulphate and chloride of copper. (Meyer.)

*Phosphate of Ethylamine and Magnesia*,  $2 \text{MgO}, (\text{C}_2\text{H}_5\text{N}, \text{HO}), \text{PO}_4 + 10 \text{Aq.}$  — Salts of ethylamine prevent the precipitation of magnesia, in the same manner as salts of ammonia; and in such a solution, phosphate of soda produces a bulky precipitate, which becomes crystalline after a while, but is much more soluble than the corresponding ammonia-salt. Analysis gave 44.63 p. c. pyrophosphate of magnesia,  $2 \text{MgO}, \text{PO}_4$ , the formula requiring 43.62 p. c. (Meyer.)

A neutral solution of sulphate of magnesia, phosphate of soda, and sulphate of ethylamine, deposits after a while, prismatic crystals, which however, soon become opaque even in the liquid, and do not redissolve. (Meyer.)

*Sulphate of Ethylamine and Alumina.* —  $(C^4H^7N,HO),Al^2O^3, 4 SO^3 + 24 Aq.$  — *Ethylamine alum.* — Obtained: 1. By mixing acid sulphate of alumina with ethylamine, redissolving the crystalline precipitate in water, and evaporating to the crystallizing point. The crystals obtained were small regular octohedrons, modified by faces of the cube. — 2. By mixing sulphate of alumina with hydrochlorate of ethylamine. The solution gave off hydrochloric acid when boiled, but did not yield any crystals even when strongly concentrated. The solution was therefore evaporated to dryness; the residual salt exhausted with absolute alcohol; the insoluble residue dissolved in water and the solution evaporated. Prismatic crystals were then obtained, resembling those of nitre; but on recrystallizing from water, the salt was obtained in regular octohedrons, an inch in diameter. Angle of the octohedron  $109^\circ 27'$  to  $109^\circ 29'$ . (Stenner & Kaumer, *Ann. Pharm.* 91, 172; Meyer.)

	Stenner & Kaumer.		Meyer.			
$Al^2O^3$ .....	51.4	...	10.68	.....	11.00	... 11.66 ... 11.18 ... 9.86
$C^4H^7N,HO$ .....	54.0	...	11.21			
$4SO^3$ .....	160.0	...	33.24	.....	33.38	... 33.92
$24HO$ .....	216.0	...	44.87	.....	45.30	
<hr/>						
$Al^2O^3(C^4H^7NO,4SO^3 + 24Aq)$	481.4	...	100.00			

A solution saturated at  $25^\circ$ , contains 1 pt. of the crystallized alum in 6.89 parts of water. (Stenner & Kaumer.)

*Sulphate of Methylamine and Alumina.* —  $(C^2H^5N,HO),Al^2O^3,4SO^3 + 24 Aq.$  — *Methylamine-alum.* — Prepared by mixing sulphate of alumina with hydrochlorate of methylamine, and purifying by recrystallization. — Regular octohedrons, about half an inch in diameter. Dihedral angles of the faces,  $109^\circ 26'$  to  $109^\circ 30'$ . (T. v. Alth, *Ann. Pharm.* 91, 171.)

	v. Alth.			
$Al^2O^3$ .....	51.4	...	11.00	..... 11.19
$C^2H^5N,HO$ .....	40.0	...	8.56	
$4 SO^3$ .....	160.0	...	34.23	..... 34.78
$24 Aq$ .....	216.0	...	46.21	..... 44.37
<hr/>				
$C^2H^5NO,Al^2O^3,4SO^3 + 24Aq$	467.4	...	100.00	

The deficiency in the water arose from efflorescence.

*Molybdate of Ethylamine.*  $C^4H^7N,HO,2MoO^3$ . — Molybdic acid dissolves readily in ethylamine, and the solution left to evaporate over chloride of calcium, deposits white scales, which become red-brown when dry, and ultimately assume a regular brown colour. Analysis gave 72.22 and 73.03 p. c.  $MoO^3$ , the formula requiring 72.23 p. c. The crystals continually give off ethylamine, and are gradually converted into a still more acid salt. (Meyer, *J. pr. Chem.* 67, 151.)

*Phospho-molybdate of Ethylamine.* — Phospho-molybdic acid produces in solutions of ethylamine, a flocculent, curdy-yellow precipitate, lighter in colour and more soluble in acids and in saline solutions, than that which the same reagent forms with ammonia. The other volatile bases and many natural alkaloids form similar precipitates. (Meyer.)

When *mercuric chloride* in excess is mixed with ethylamine, a white precipitate is produced, which continually loses mercury during washing. Its analysis gave 75.03 p. c. mercury, and 15.21 chlorine, agreeing nearly with the formula  $4\text{HgCl} + \text{N.C}^4\text{H}^5, \text{H}, \text{Hg} + 2\text{HgO}$  (calc. 75.06 Hg and 15.18 Cl). — If the ethylamine is added in excess, a yellow flocculent precipitate is formed, which gives by analysis 85.65, p. c. Hg, 8.52 Cl, 1.88 C, 0.34 H, 0.80 N, and 3.31 O, from which it is not possible to deduce any rational formula. *Biethylamine* and *triethylamine* yield similar precipitates with mercuric chloride. *Hydrate of tetrethylum* added to mercuric chloride, throws down pure mercuric oxide, or if carbonic acid is present, an oxychloride. (Meyer.)

Page 65.

### Tetrethylum, &c.

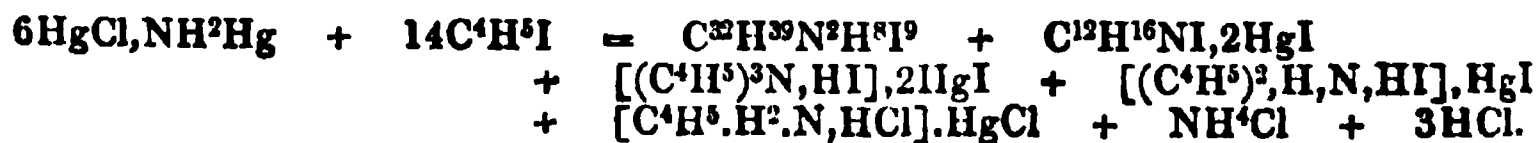
SONNENSCHN. *Ann. Pharm.* 101, 20.

When white precipitate,  $\text{HgCl}, \text{NH}^2\text{Hg}$ , triturated with water, is mixed with  $1\frac{1}{2}$  pt. of iodide of ethyl, and heated for several days in the water-bath, there are formed, without evolution of gas, golden-yellow crystals (*a*) surrounded with a heavy dark brown liquid (*b*), above which floats a nearly colourless watery solution (*c*). This watery solution contains mercuric chloride, sal-ammoniac, and a crystallizable compound of mercuric chloride and hydrochlorate of ethylamine. The dark brown liquid (*b*) solidifies in a crystalline mass after the excess of iodide of ethyl has been driven off; the solution of this substance in a mixture of alcohol and ether, deposits large yellow needles consisting of double salts of mercuric iodide with the hydriodates of ethylamine, biethylamine, and triethylamine; and the oily mother-liquor ultimately yields crystals of iodide of mercury and tetrethylum.

The yellow crystals (*a*), after being purified by washing with warm absolute alcohol, resemble mosaic gold, and appear under the microscope as cubes with octohedral and dodecahedral faces. They are decomposed by sunlight, with separation of *mercury*, melt at  $150^\circ$ , and decompose at higher temperatures. They are insoluble in water, alcohol, and ether. Analysis shows them to be composed of  $\text{C}^{32}\text{H}^{39}\text{N}^3\text{Hg}^8\text{I}^9$ .

Yellow Crystals.				Sonnenschein.			
32 C.....	192	....	8.72	.....	7.98	to	8.78
39 H .....	39	....	1.77	.....	1.42	„	1.79
2 N .....	28	....	1.27	.....	1.20	„	1.45
8 Hg .....	800	....	36.37	.....	34.78	„	36.85
9 I .....	154	....	51.87	.....	49.12	„	52.65
$\text{C}^{32}\text{H}^{39}\text{N}^3\text{Hg}^8\text{I}^9$ .....				1213	....	100.00	

This formation of these crystals, together with that of the compounds previously mentioned, may be represented by the equation:



They may be regarded as a compound of mercuric iodide with iodide of tetrethylum and *iodide of mercurotetrethylum*,  $C^{16}H^{19}HgN,I$ :



Iodide of potassium and iodide of tetrethylum dissolve the compound for the most part, with separation of metallic mercury. — Nitric acid separates mercuric iodide. Its solution in hot hydrochloric acid yields greenish yellow silky crystals. — Chlorine and bromine separate all the iodine after some time, forming crystals with a jetty lustre resembling naphthalin. — When the yellow crystals are heated with recently precipitated oxide of silver, iodide of silver is formed, together with a strongly alkaline liquid, which, after the excess of silver has been removed by sulphuretted hydrogen, contains hydrate of tetrethylum. (On neutralising with hydrochloric acid and adding bichloride of platinum, a precipitate was formed containing 28.24 p. c. C, 5.95 H, 4.19 N, and 29.6 Pt, the formula  $C^{16}H^{20}NCl.PtCl^2$  requiring 28.66 C, 5.97 H, 4.18 N, and 29.42 Pt. — But if the alkaline solution is neutralised with hydrochloric acid without previous treatment with sulphuretted hydrogen, and evaporated, white crystals are obtained, consisting of a compound of mercuric chloride with chloride of tetrethylum :

Sonnenschein.					
$C^{20}H^{16}N$ .....	150	.....	43.18	....	43.32
Hg .....	200	.....	33.25	....	33.96
2 Cl .....	71	.....	23.57	....	23.12
<hr/>					
$C^{20}H^{16}NCl + HgCl$ ....	421	.....	100.00	....	100.40

The amount of tetrethylum ( $C^{20}H^{16}N$ ) was determined by forming the platinum-salt, and weighing the platinum left on ignition. (Sonnenschein.)

A solution of *sulphate of tetrethylum* mixed with cyanate of potash and evaporated, yields, when the residue is extracted with alcohol, not tetrethylurea, but carbonate of tetrethylum. (A. Brünig, *Ann. Pharm.* 104, 200.)

*Iodide of Tetrethylum and Mercury.* — a.  $(C^4H^5)^4NI,2HgI$ . — Produced by the action of metallic mercury on teriodide of tetrethylum (ix, 67):



The compound dissolves sparingly in water, more easily in hot alcohol, from which it separates on cooling in light yellow, shining, scaly crystals. (H. Risse, *Ann. Pharm.* 107, 224.)

Risse.					
16 C .....	96	...	13.50		
20 H .....	20	...	2.81		
N .....	14	...	1.97		
2 Hg .....	200	...	28.18	.....	28.44
3 I .....	381	...	53.59	.....	53.85
<hr/>					
$(C^4H^5)^4NI,2HgI$ .....	711	...	100.00		

b.  $(C^4H^5)^4NI, 3HgI$ . — Produced by the action of trimercuramine on iodide of ethyl:



It is best to use trimercuramine containing a little mercuric oxide; pure trimercuramine is too dangerously explosive.

Yellow crystals, which dissolve pretty readily in alcohol, and are not decomposed by water. (R. Müller, *Ann. Pharm.* 108, 6.)

Müller.					
16 C .....	96	...	10.23		
20 H .....	20	...	2.13		
N .....	14	...	1.49		
3 Hg.....	300	...	31.99	.....	31.04
4 I .....	508	...	54.16	.....	23.80
<hr/>					
$(C^4H^5)^4NI, 3HgI$ ....	938	...	100.00		

*Teriodide of Trimethylethylum*,  $(C^3H^3)^3, C^4H^5, N, I^3$ . — Produced by the action of 2 at. iodide on 1 at. protiodide of trimethylethylum in hot alcoholic solution, and separates on cooling in brittle rhombic prisms, which are instantly decomposed by water into the pentaiodide and protiodide of trimethylethylum:



In alcoholic solution, on the contrary, the pentaiodide and protiodide immediately unite and form the teriodide. — This compound melts at  $64^\circ$  without decomposition. The crystals are dark brown, in their fragments brownish yellow and somewhat dichromatic: surface-colour bluish violet. (R. Müller, *Ann. Pharm.* 108, 1.)

Müller.					
10 C .....	60	...	12.79	.....	12.54
14 H .....	14	...	2.98	.....	3.12
N .....	14	...	2.98		
3 I .....	381	...	81.25	.....	80.91
<hr/>					
$(C^3H^3)^3, C^4H^5, N, I^3$ .....	465	...	100.00		

*Pentaiodide of Trimethylethylum*,  $(C^3H^3)^3, C^4H^5, N, I^5$ . — Obtained by the action of iodine in excess on the protiodide or teriodide of trimethylethylum, or as above mentioned, by the action of water on the teriodide. Crystallizes in quadratic laminæ, having a metallic lustre and splendid greenish iridescence, oP.  $\infty$  P  $\infty$ . P. (the P faces very little developed). oP:P =  $141^\circ$ . The crystals are opaque; yellowish in thin layers when polished, yellowish brown in thicker layers; surface-colour metallic green, becoming dark blue on exposure to the air. They melt at about  $68^\circ$ .

Müller.					
10 C .....	60	...	8.30	.....	8.17
14 H .....	14	...	1.94	.....	2.34
N .....	14	...	1.94		
5 I .....	635	...	87.82	.....	87.85
<hr/>					
$(C^3H^3)^3, C^4H^5, N, I^5$ ....	723	...	100.00	.....	100.00

*Teriodide of Triethylmethylium*,  $\text{C}^3\text{H}^3(\text{C}^4\text{H}^5)^3\text{NI}^3$ . — Prepared in the same manner as the preceding compounds. Crystallizes in bluish violet square laminæ, which appear dark red by transmitted light, and melt at  $62^\circ$ .

					Müller.
14 C	.....	84	...	16.90	
18 H	.....	18	...	3.62	
N	.....	14	...	2.82	
3 I	.....	381	...	76.66	..... 76.38
<hr/>					
$\text{C}^3\text{H}^3, (\text{C}^4\text{H}^5)^3, \text{NI}^3$	....	497	....	100.00	

There is no pentaiodide of triethylmethylium.

All these compounds form with mercury, compounds analogous to those prepared by Risse (p. 483).

*Teriodide of Trimethylamylum*,  $(\text{C}^3\text{H}^3)^3\text{C}^{10}\text{H}^{11}\text{N}, \text{I}^3$  — Obtained by heating trimethylamine and iodide of amyl for some time to  $160^\circ$ , and treating the product with tincture of iodine. — Crystallizes in dark brown flattened rhombic prisms, easily soluble in alcohol, nearly insoluble in water. Combination:  $\infty \text{P} : \infty \bar{\text{P}}$  (often predominating)  $\infty \bar{\text{P}} : \infty \text{P} : \frac{1}{2} \bar{\text{P}}$ . — Inclination of the faces,  $\infty \text{P} : \infty \text{P} = 104^\circ 28'$ ;  $\bar{\text{P}} : \bar{\text{P}} = 112^\circ 24'$ . — The crystals exhibit trichroism when viewed in such a manner that, when the crystal is set upright the light, may pass through them at right angles to  $\infty \bar{\text{P}}$ , the ordinary ray is dark brown, or nearly black, and the extraordinary ray light red-brown, the third tint being intermediate between the two. Melting point  $80^\circ$ . (R. Müller, *Ann. Pharm.* 108, 4.)

					Müller.
16 C	.....	96	...	18.79	
20 H	.....	20	...	3.91	
N	.....	14	...	2.74	
3 I	.....	381	...	74.56	..... 74.56
<hr/>					
$(\text{C}^3\text{H}^3)^3, \text{C}^{10}\text{H}^{11}, \text{N}, \text{I}^3$	....	511	....	100.00	

The pentaiodide does not appear to exist.

### Ethylene-bases.

Cloez, in 1843 (*Institut*, 1853, 213), by heating alcoholic ammonia in sealed tubes with bromide or chloride of ethylene, obtained three volatile bases, which he supposed to contain the radicals  $\text{C}^3\text{H}$ ,  $\text{C}^4\text{H}^3$ ,  $\text{C}^6\text{H}^5$ , viz., *formylia*,  $\text{C}^3\text{H}^3\text{N} = \text{C}^3\text{H}, \text{H}^3\text{N}$ ; *acetylia* (vinylamine),  $\text{C}^4\text{H}^5\text{N} = \text{C}^4\text{H}^3, \text{H}^2\text{N}$ ; and *propylia*,  $\text{C}^6\text{H}^7\text{N} = \text{C}^6\text{H}^5, \text{H}^2\text{N}$ . The second of these has also been obtained by Natanson (xii, 548).

These bases have lately been examined by Hofmann (*Proc. Roy. Soc.* ix, 154), who takes a different view of their constitution, regarding them as *biamines*, i.e., as bases derived from a double molecule of ammonia, by the substitution of a biatomic radical (ethylene) for 2 atoms of hydrogen. It is difficult indeed to understand how the action of ammonia on an ethylene-compound can produce bodies containing three different radicals, as Cloez supposes. Moreover, the high boiling points of these bases



and the differences between these boiling points, are in favour of Hofmann's view. It will be remembered that methylamine, which contains 2 at. H more than formylia, is a gas at ordinary temperatures, and liquefies considerably below the freezing point of water. Again, the differences between the boiling points of substances related, as the formulæ of Cloez suppose, do not generally exceed 20°, and very rarely rise to 40° or 47°. The following table exhibits the formulæ of these bodies as they are regarded by Cloez and by Hofmann, together with the boiling points:

	Cloez.	Hofmann.	B. P.	Diff.
Formylia	.... $C^2H^3N$ .....	$(C^4H^4), H^1, N^2$ .....	123	} 47°
Acetylia	.... $C^4H^5N$ .....	$(C^4H^4)^2, H^2, N^2$ .....	170	
Propylia	.... $C^6H^7N$ .....	$(C^4H^4)^3, N^2$ .....	210	} 40

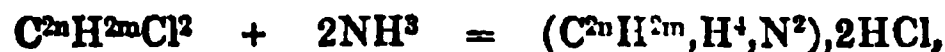
According to Hofmann's formulæ, the first base is *ethylene-biamine*, the second *biethylene-biamine*, and the third *triethylene-biamine*. These bases are rapidly attacked by bromide of ethylene, the product being a non-volatile body, probably containing the fourth number of the series, *tetrethylene-biammonium*  $(C^4H^4)^4N^2$ .

The analysis of the hydrochlorate of the so-called formylia, and of the base separated from it by the action of an alkali — which base contains the elements of water not separable by caustic baryta — agree much better with Hofmann's formulæ than with those of Cloez:

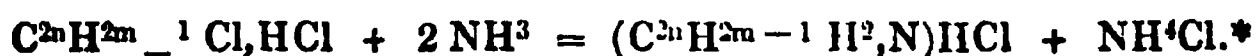
Hydrochlorate.	Calculation.				Analyses.	
	$C^2H^3N, HCl$		$C^4H^5N^2, H^2Cl^2$		Cloez.	Hofmann.
Carbon	..... 18.32	....	18.04	.....	17.56	.... 17.87
Hydrogen	..... 6.11	....	7.52	.....	7.39	.... 7.55
Nitrogen	..... 21.37	....	21.06	.....	20.47	
Chlorine	..... 54.20	....	53.38	.....	53.62	.... 53.17
	100.00	....	100.00			

Free base.	Calculation.				Analyses.	
	$C^2H^3N, HO$		$C^4H^5N^2, H^2O^2$		Cloez.	Hofmann.
Carbon	..... 31.58	....	30.76	.....	31.12	.... 30.67
Hydrogen	..... 10.52	....	12.82	.....	12.78	.... 12.97
Nitrogen	..... 36.84	....	35.90	.....	35.80	.... 36.32
Oxygen	..... 21.06	....	20.52	.....	20.30	.... 20.04
	100.00		100.00			

On the other hand, Cloez points out (*Compt. rend.* 46, 344), that according to Hofmann's view of the formation of these bases, which may be represented by the general equation:



no chloride of ammonium should be formed in the reaction, whereas experiment shows that this salt is produced, and consequently that the reaction may be more correctly represented by the formula:



The vapour-density of the hydrated base  $C^2H^4NO$ , is also adduced by Cloez as an argument — and the principal one — in support of his formula. This vapour-density he finds by experiment to be 1.427; now,

\* See note to page 488.

for a condensation to 2 volumes, the formula  $C^2H^4NO$  gives as the calculated density, 1·317, whereas Hofmann's formula,  $C^4H^{10}N^2O^2$ , gives 2·706.

	Vol.	Density.		Vol.	Density.
C-vapour .....	2	0·8320	C-vapour .....	4	1·6640
H-gas .....	4	0·2772	H-gas .....	10	0·6930
N-gas .....	1	0·9706	N-gas .....	2	1·9412
O-gas .....	$\frac{1}{2}$	0·5546	O-gas .....	1	1·1093
Vapour of $C^2H^4NO$ .....	2	2·6344	Vapour of $C^4H^{10}N^2O^2$ ....	2	5·4075
	1	1·3172		1	2·7057

To render the vapour-density calculated from the latter formula conformable with the experimental determination, it is necessary to suppose, either that the formula  $C^4H^{10}N^2O^2$  represents 4 volumes of vapour, which is not in accordance with the general law, or else that the molecule  $C^4H^{10}N^2O^2$  splits up at high temperatures into  $C^4H^8N$  and  $H^2O^2$ , each of which, in the state of vapour, occupies two volumes (see note to page 411).

There are several other compounds which exhibit the same apparent anomaly of vapour-volume, and may be supposed in like manner to resolve themselves, at the high temperature at which the vapour-density is determined, into *two vapours*, each occupying two volumes, so that the whole appears as a four-volume gas; the two substances however reuniting as the vessel cools, and reproducing the original compound, so that there is no direct evidence of the decomposition having taken place. A decomposition of this kind is actually observed in iodide of tetrethylum,  $N(C^4H^5)_4I$ , which, when rapidly heated to a high temperature, splits up into triethylamine  $N(C^4H^5)_3$  and iodide of ethyl  $C^4H^5I$ , which at first form two distinct layers in the receiver, but quickly unite and reproduce the original compound. (Hofmann, ix, 67).

The following table exhibits the vapour-densities of these substances as determined by experiment and calculation, together with the manner in which they may be supposed to split up at high temperatures.

Substance.	Vapour-density.		
	Experiment.	Theory. 2 vol.	Theory. 4 vol.
Chloride of ammonium $NH^4Cl = NH^3 + HCl$ }	0·890	1·850	0·925
Pentachloride of phosphorus $PCl^5 = PCl^3 + Cl^2$ }	3·654	7·214	3·624
Sulphydrate of ammonium $NH^4S, HS = NH^3 + 2HS$ }	0·884	1·765	0·882
Tellurhydrate of ammonium $NH^4Te, HTe = NH^3 + 2HTe$ }	1·320	2·840	1·420
Oxide of biethylene-biammonium* $C^{12}H^{18}N^2O^2 = C^{12}H^{16}N + 2HO$ }	2·260	4·620	2·310

\* Obtained by treating ethylamine with bibromide of ethylene, and decomposing the resulting bromide  $\{(C^4H^4)', (C^4H^5)^2, H^4\}, Br^2$ , with baryta water. (Hofmann, *Proc. Roy. Soc.* 10, 107.)

The argument founded upon the vapour-density cannot therefore be considered as conclusive in favour of the formulæ proposed by Cloez.\*

The bromides of propylene, butylene, amylene, and caprylene also yield basic compounds when heated with alcoholic ammonia. In the case of propylene, the results vary somewhat, according as that gas has been prepared from amylic alcohol or from glycerine by Berthelot's process. (Cloez, *Compt. rend.* 46, 344.)

### Tetravinylum. $C^{16}H^{12}N = N(C^4H^3)^4$ .

V. BABO. *J. pr. Chem.* 72, 88.

HEINTZ & WISLICENUS. *J. pr. Chem.* 76, 116; *Pogg. Ann.* 105, 577.

*Tetracetylum, Tetracetosylum, Tetrellallylammonium.*

Formed by the decomposition of aldehyde-ammonia at high temperatures. Not known in the separate state. The hydrated oxide and several of the salts were first prepared and analysed in an impure state by Babo; afterwards obtained in greater purity and more completely examined by Heintz & Wislicenus.

*Preparation of the Hydrated Oxide,  $C^{16}H^{12}NO,HO$ .* — Aldehyde-ammonia not quite dry, is heated at the temperature of the water-bath in a flask having a long vertical condensing tube. Ammonia then escapes, while water and aldehyde-ammonia are condensed and flow back again, and at length the base remains as a syrupy, brown, bitter mass, which when quite dry is brittle and resinous. It is purified by dissolving it in sulphuric acid; precipitating the sulphate by strong alcohol; dissolving in water; precipitating the base by caustic potash; collecting the resulting brown flakes in a filter; dissolving them in alcohol; passing carbonic acid through the alcoholic solution, whereby the remaining potash is precipitated as carbonate, while the organic base remains free; filtering again; evaporating to complete dryness; dissolving out the base with absolute alcohol; and repeating the whole series of operations three or four times. (Heintz & Wislicenus.)

The formation of the base may be represented by the following equation:



Babo, by heating aldehyde-ammonia in a sealed tube to 120° for several hours, and distilling off the more volatile portion of the product, obtained a brown amorphous mass, having a slight alkaline reaction, soluble in acids, and forming brown resinous precipitates with bichloride of platinum, chromic acid, and tannic acid. The platinum-

\* Since the above was printed, Dr. Hofmann has published a paper (*Proc. Roy. Soc.*, 10, 224) containing additional facts in confirmation of his views. In particular, it must be mentioned, that he has found the vapour-density of the anhydrous base to be 2.00. Now, according to the formula  $(C^4H^4),H^4,N^2$ , referred to two volumes, it should be 2.07, whereas, according to the formula,  $C^2H,H^2N$ , it should be 1.00. — Hofmann also points out that the formation of the bases containing 2 or more At. ethylene is necessarily accompanied by the formation of chloride of ammonium: e.g.



salt prepared from a portion of the base which had been purified by repeatedly precipitating the sulphate with alcohol, &c., gave results agreeing with the formula  $C^{16}H^{12}NO, HCl, PtCl^2$ , or  $N(C^4H^3)^4Cl, PtCl^2 + HO$ .

*Hydrated oxide of Tetravinylum*, obtained by evaporation of the alcoholic solution, is a resinous, perfectly amorphous, brittle, fissured mass, having a bitter taste; red-brown by transmitted light, somewhat darker and with a tinge of violet by reflected light, and exhibiting a strong lustre on the surface and when fractured. It yields a yellow-brown powder.

				Heintz & Wislicenus.	
16 C .....	96	....	69.07	.....	69.11
13 H .....	13	....	9.35	.....	9.36
N .....	14	....	10.07	.....	10.10
2 O .....	16	....	11.51	.....	11.43
<hr/>					
$(C^4H^3)^4NO, HO$ .....	139	....	100.00	.....	100.00

The base decomposes at  $180^\circ$ , after previous fusion, giving off volatile empyreumatic products and leaving a black, shining charcoal. — Among the volatile products is a strongly basic oil which dissolves in alcohol and in acids, and appears to consist of at least two bodies, which could not be separated on account of the smallness of the supply of material, and the facility with which the oil decomposed into ammonia and brown-black insoluble powder, especially in presence of acids. The oil probably contains *trivinylamine*,  $N(C^4H^3)^3$ .

Hydrate of tetravinylum dissolves very sparingly in water, rather more in cold than in warm water, the solution frothing like soap-suds. It dissolves in alcohol in all proportions, but is insoluble in ether. The solutions have a faint but distinct alkaline reaction. It is difficult to free the hydrate from the last traces of hygroscopic water. (Heintz & Wislicenus.)

With acids, excepting carbonic acid, it unites readily, forming salts which are for the most part easily soluble in water but insoluble in alcohol.

The *neutral sulphate*,  $C^{16}H^{12}N, SO^4$ , obtained by mixing the alcoholic solution of the base with sulphuric acid diluted with alcohol, in quantity not quite sufficient for a complete precipitation, forms when dry, a dark brown, uncrystallizable, non-deliquescent mass.

				Heintz & Wislicenus.	
16 C .....	96	....	56.47	.....	56.52
12 H .....	12	....	7.06	.....	7.35
N .....	14	....	8.21		
O .....	8	....	4.73		
$SO^3$ .....	40	....	23.53	....	23.37
<hr/>					
$C^{16}H^{12}N, SO^4$ .....	170	....	100.00		

An *acid sulphate*,  $2(C^{16}H^{12}N, SO^4) + SO^4H$ , is obtained by treating the solution of the base with excess of sulphuric acid. It has a foxy-red colour and strong lustre. Contains 30.64 p.c.  $SO^3$  (calculated quantity, 33.85). (H. & W.)

The *chloride*,  $C^{16}H^{12}NCl + HO$ , obtained by dissolving the base in hydrochloric acid and evaporating, is an uncrystallizable, very hygroscopic, shining mass, having a dark brown colour, with strong violet iridescence.

<i>Dried between 120° and 140°.</i>				<i>Heintz &amp; Wislicenus.</i>	
16 C .....	96.0	....	57.66	.....	57.69
13 H .....	13.0	....	7.81	.....	7.77
N .....	14.0	....	8.41		
Cl .....	35.5	....	21.32	.....	21.48 .... 21.23
O .....	8.0	....	4.80		
<hr/>					
$C^{16}H^{12}NCl + Aq.$	166.5	....	100.00		

The *chloroplatinate*,  $(C^4H^3)^4NCl, PtCl^3$ , is obtained as a yellowish-brown amorphous precipitate, by mixing the solution of the hydrochlorate with bichloride of platinum. When dried at 150°, it gives by analysis 30.56, 30.65, and 30.68 p. c. platinum, the formula requiring 30.14 p. c. Dried between 110° and 120°, it retains an atom of water; for it then gives by analysis 29.09 p. c. platinum, the formula  $C^{16}H^{12}NCl.PtCl^2 + HO$  requiring 29.33 p. c. (Heintz & Wislicenus.) This hydrated platinum-salt was first obtained by Babo (p. 488), not, however, in a perfectly pure state; for his analysis gave only 28.9 and 28.5 p. c. platinum.

The *chloro-aurate* is a precipitate of similar character, but it decomposes at the boiling heat, yielding metallic gold in microscopic octohedrons. — The solution of chloride of tetravinylium forms with *mercuric chloride* a dark brown, amorphous, flocculent precipitate, which dissolves to a very small amount in boiling water, but separates again on cooling. (Heintz & Wislicenus.)

The *neutral oxalate*,  $C^4(C^{16}H^{12}N)^3O^8$ , is precipitated on mixing the alcoholic solutions of the acid and base, the latter being in excess: it resembles the sulphate in appearance.

				<i>Heintz &amp; Wislicenus.</i>	
36 C .....	216	....	65.06	.....	65.20
24 H .....	24	....	7.23	.....	7.37
2 N .....	28	....	8.43		
8 O .....	64	....	19.28		
<hr/>					
$C^4(C^{16}H^{12}N)^3O^8$	332	....	100.00		

An *acid oxalate* is obtained by treating the base with excess of oxalic acid: it is very deliquescent, and dissolves readily in alcohol. (Heintz & Wislicenus.)

*Tartrate of Tetravinylium* is insoluble in alcohol. The *tannate* is insoluble, even in water. (Heintz & Wislicenus.)

The compounds just described cannot be represented as containing a biatomic radical, without introducing hypotheses quite unsupported by experiment. They all contain 16 At. carbon to 1 At. nitrogen; hence, to represent them as ammonium-compounds containing a biatomic radical, we must suppose them to contain butylene  $C^8H^8$ , making the formula of the chloride  $N(C^8H^8)^2Cl + HO = C^{16}H^{17}NClO$ , and that of the hydrated oxide  $N(C^8H^8)^2O + HO = C^{16}H^{17}NO^2$ . Now it is very improbable that a butylene-compound should be formed from aldehyde-ammonia, and moreover, the composition, as calculated from these formulæ, deviates widely from the experimental results. Thus, the formula  $C^{16}H^{17}NClO$ , gives for the hydrated chloride, 56.30 p. c. C, 9.97 H, and 20.82 Cl, the carbon being 1.39 p. c. below, and the hydrogen 2.2 p. c. above the quantities found by experiment. The formula proposed by the discoverers must therefore be retained.

Sodium-ethyl.  $C^4H^5Na$ .

J. A. WANKLYN. *Ann. Pharm.* 107, 125 ; 108, 67. *Chem. Soc. Qu. J.* 11, 108.

Obtained in combination with zinc-ethyl, by the action of sodium on zinc-ethyl; it has not yet been obtained in the separate state. When a piece of sodium is introduced, together with about ten times its weight of zinc-ethyl, into a glass tube previously filled with coal-gas, and the tube then sealed, left to stand in cold water, and occasionally shaken, the sodium gradually dissolves without evolution of gas; an equivalent quantity of zinc is precipitated; and after a few days, the tube contains nothing but metallic zinc, and a colourless, highly inflammable liquid, which, on coming in contact with the air, burns with explosive rapidity, and leaves a strongly alkaline residue. This liquid consists of a compound of sodium-ethyl and zinc-ethyl dissolved in excess of zinc-ethyl. On cooling the liquid to  $0^\circ$ , the compound separates in rhombic tables; and on evaporating the liquid in a stream of hydrogen-gas, as long as zinc-ethyl continues to pass off, the same compound remains as a crystalline mass, which melts at  $27^\circ$ .

This compound of sodium-ethyl and zinc-ethyl could not be exactly analysed, on account of its great tendency to oxidise; but it appears to consist of  $C^4H^5Na + 2 C^4H^5Zn$ . When decomposed by water, it yields hydride of ethyl, soda, and oxide of zinc. The proportion of zinc to sodium was found to be 28.20 Zn to 12.89 Na (nearly 2 At. to 1 At.), and about 47.60 pts. of hydride of ethyl were evolved to 7.6 pts. sodium, the formula requiring 50.3 pts.

Sodium-ethyl cannot be obtained from this compound in the free state. On attempting to distil off the zinc-ethyl, gas is evolved and metallic sodium remains, together with zinc; similarly when the compound is heated with potassium or sodium at the temperature of the water-bath. Neither can sodium-ethyl be obtained by the action of sodium on iodide of ethyl or ether. Sodium does not act perceptibly on either of these liquids separately, even with the aid of heat, and with a mixture of the two, either in the cold or at  $100^\circ$ , it forms a blue modification of iodide of sodium, but no sodium-ethyl, because, according to Frankland (*Ann. Pharm.* 110, 107), that compound, in contact with iodide of ethyl, is immediately decomposed, forming iodide of sodium and giving off a mixture of hydride of ethyl and ethylene:



Sodium-ethyl (in the form of the compound above described) is attacked by carbonic acid gas with considerable evolution of heat, and converted into propionate of soda:



[Sodium-methyl treated in the same manner yields acetate of soda (p. 442)]. — Sodium-ethyl is also acted upon by carbonic oxide and by cyanogen; but the products have not yet been satisfactorily examined.

Potassium acts on zinc-ethyl even more energetically than sodium, and forms a similar compound of zinc-ethyl with potassium-ethyl, from

which the latter cannot be separated. *Lithium* also forms a similar compound. *Calcium* appears to act immediately on zinc-ethyl; *magnesium* not at all, even at 100°. (Wanklyn.)

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*Compounds of Alcohol-radicals with the Earth-metals.*—Magnesium, in the state of coarse powder, decomposes iodide of ethyl even at ordinary temperatures, more quickly when heated with it in a sealed tube, forming iodide of magnesium, gaseous products, and a colourless volatile liquid, which has a penetrating alliaceous odour, is not spontaneously inflammable, but forms thick white fumes of magnesia in contact with the air, and decomposes water with violence. This liquid is probably *magnesium-ethyl*.—*Aluminium* decomposes iodide of ethyl in like manner, forming a spontaneously inflammable liquid, probably *aluminium-ethyl*, which, when distilled in a stream of carbonic acid, yields a heavy colourless oil of very high boiling point, and likewise capable of decomposing water with violence. Pulverized *vanadium* slowly attacks iodide of ethyl at 180°, yielding a deep red liquid. (Hallwachs & Schafarik, *Ann. Pharm.* 109, 206.)

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Page 70.

### Ethyl and Methyl-bases containing Arsenic and Phosphorus.

CAHOUS. *Compt. rend.* 49, 87. *Ann. Pharm.* 112, 228.

When arsenide of zinc or cadmium is introduced into sealed tubes, together with iodide of methyl, and the mixture heated to 175° or 180°, the iodide of methyl disappears completely, and a greyish solid coherent mass is formed, which dissolves pretty freely in boiling alcohol. On evaporating the alcoholic liquid, fine, colourless prismatic crystals are obtained, having a strong lustre, and consisting of  $(C^2H^3)^4AsI, ZnI$ , and  $(C^2H^3)^4AsI, CdI$ . If the zinc-compound be thrown into boiling potash, the zinc is dissolved, and a heavy oil separates, which soon solidifies on cooling. On pulverizing this substance, and leaving it in contact with the air for 24 hours, the potash which it contains is converted into carbonate; and if the product be then digested in absolute alcohol, a solution is obtained, which by evaporation, yields beautiful colourless prisms of *iodide of arsemethylum*  $(C^2H^3)^4AsI$ .

With iodide of ethyl, compounds are formed isomorphous with the preceding, and containing:



Free arsenic, with the iodides of ethyl and methyl, yields in like manner:





and these products treated with a boiling solution of strong potash, yield arsenite of potash, iodide of potassium, and the iodides of arsenmethylium and arsenethylium.

If instead of proceeding as above, the mixture be evaporated to dryness, and distilled in an apparatus filled with hydrogen or carbonic acid, oily products collect in the receiver, having the odour of arsenietted hydrogen, and consisting of pure *arsentrimethyl* or *arsentriethyl*.

The preparation of the double iodides above mentioned, affords the best means of obtaining the compounds  $(C^2H^3)^3As$ ,  $(C^2H^3)^4As$ ,  $(C^4H^5)^3As$ , and  $(C^4H^5)^4As$ .

When arsentrimethyl is treated with iodide of ethyl, or arsentriethyl with iodide of methyl, compounds are produced isomorphous with the iodides of arsenmethylium and arsenethylium, and composed of:



Pure arsentrimethyl is a colourless, very mobile liquid, which boils above  $100^\circ$ . It forms with oxygen a very deliquescent compound,  $(C^2H^3)^3AsO^2$ , yielding by exposure in vacuo, beautiful crystals, which quickly liquefy in contact with the air. With sulphur, arsentrimethyl forms splendid colourless prisms  $(C^2H^3)^3AsI^2$ , which are obtained very well defined, by slow evaporation of the aqueous or alcoholic solution. It unites also with iodine and bromine, forming the compounds  $(C^2H^3)^3AsI^2$  and  $(C^2H^3)^3AsBr^2$ .

Crystallized phosphide of zinc (obtained by heating the metal to saturation with vapour of phosphorus, in a current of hydrogen), acts on the iodides of methyl and ethyl at  $180^\circ$ , in the same manner as the arsenide, yielding similar products. On exhausting the product with boiling alcohol, and evaporating over the water-bath, yellow spongy products are obtained; and on treating these products with a small quantity of dilute alcohol, a solution is obtained, which, when left to evaporate in vacuo, deposits beautiful amber-coloured crystals, isomorphous with those produced with arsenide of zinc; and on treating these crystals with hot potash-ley, heavy oils separate, which solidify on cooling, and dissolve readily in alcohol. The liquid when evaporated, deposits beautiful colourless needles of *iodide of phosphomethylium* or *phosphethylium*,  $(C^2H^3)^4PI$ , and  $(C^4H^5)^4PI$ . These products are decomposed by distillation, yielding *trimethylphosphine*  $(C^2H^3)^3P$ , and *triethylphosphine*  $(C^4H^5)^3P$ ; and these compounds treated with iodide of methyl or iodide of ethyl, reproduce the *iodides of phosphomethylium* and *phosphethylium*.

The iodides of methyl and ethyl act strongly in sealed tubes on free antimony and antimonide of zinc; and the products distilled with lumps of potash yield stibmethyl and stibethyl; but they are viscid and difficult to purify.

It appears then, that when the iodides of methyl and ethyl are heated with bodies of the phosphorus family, the compounds which have the greatest tendency to form, are the iodides of phosphethylium, arsenethylium, &c., which may be represented by the general formula  $RMe^4I$  and  $REt^4I$ .



## Cacodyl-compounds.

A. BAEYER. *Ann. Pharm.* 107, 257.

*Terchloride of Cacodyl*,  $\text{As}(\text{C}^2\text{H}^3)^2\text{Cl}^3$ . — Produced by the action of pentachloride of phosphorus on cacodylic acid (ix, 327).



1. To moderate the action, the chloride of phosphorus is immersed in anhydrous ether, and pulverised cacodylic acid is added in successive small portions; hydrochloric acid is then evolved, and terchloride of cacodyl separates in crystalline laminæ, which are washed with anhydrous ether, and then recrystallized from ether, care being taken to preserve them from the smallest trace of moisture. Oxychloride of phosphorus may be substituted for the pentachloride, but the action does not go on so well, even when ether is added. — 2. By the action of chlorine gas on protochloride of cacodyl (ix, 343). If the gas be passed directly into the protochloride of cacodyl, the liquid takes fire, and complete decomposition ensues; but when it is made to flow on the surface of a mixture of protochloride of cacodyl and bisulphide of carbon, it is absorbed, and the terchloride separates in crystalline laminæ.

Terchloride of cacodyl crystallizes from its ethereal solution, by slow evaporation in transparent colourless prisms, which generally lose their lustre in vacuo; from solution in bisulphide of carbon—in which it is less soluble than in ether,—it separates in large laminæ. When prepared from cacodylic acid, it decomposes readily, becoming liquid in the course of a day, even when kept in sealed tubes, and giving off a large quantity of gas; but when prepared from protochloride of cacodyl, it is more stable, and at low temperatures may be preserved unchanged for a considerable time.

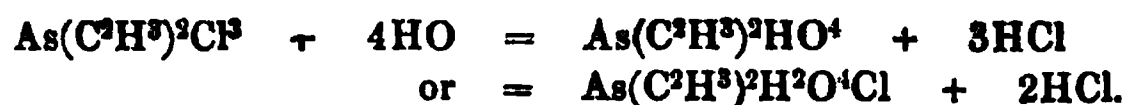
				Baeyer.
4 C .....	24.0	...	11.35	..... 11.46
6 H .....	6.0	...	2.84	..... 3.05
As .....	75.0	...	35.06	
3 Cl .....	106.5	...	50.35	..... 49.45
<hr/>				
$\text{As}(\text{C}^2\text{H}^3)^2\text{Cl}^3$ .....	211.5	...	100.00	

The formation of this compound from cacodylic acid by the action of  $\text{PCl}^5$ , leads to the supposition that cacodylic acid is a quadribasic acid  $\left. \begin{array}{c} \text{AsMe}^3 \\ \text{H} \end{array} \right\} \text{O}^4$ , containing the teratomic radical  $\text{As}(\text{C}^2\text{H}^3)^2$ . (Baeyer.)

*Decompositions.* 1. Terchloride of cacodyl is decomposed by a heat of  $40^\circ$  or  $50^\circ$ , into chloride of methyl and chloride of *arsenmonomethyl* :



2. It is decomposed by water, forming hydrochloric acid, and either cacodylic acid or basic perchloride of cacodyl (ix, 347) ;



The former decomposition takes place when there is sufficient water present to dissolve the products; the latter, when the terchloride is exposed to moist air, or when a small quantity of water is added to its ethereal solution. — 3. With absolute alcohol, it forms basic perchloride of cacodyl and chloride of ethyl:



The basic perchloride of cacodyl produced by these reactions, gave by analysis 13.55 p. c. C, 4.69 H, and 20.6 to 21.0 Cl, the formula  $\text{As}(\text{C}^2\text{H}^3)^2\text{H}^2\text{O}^4\text{Cl}$ , requiring 13.75 C, 4.58 H, and 30.34 Cl. These results show that the true formula of the basic perchloride, is that originally determined by Bunsen, not that proposed by Gmelin (ix, 347). — 4. The ethereal solution of terchloride of cacodyl, does not attack mercuric oxide; but on addition of alcohol, a brisk action takes place, and an oil is separated containing chlorine and mercury; on adding a larger quantity of mercuric oxide, the whole solidifies in a mass consisting of mercuric chloride, and the compound  $\text{As}(\text{C}^2\text{H}^3)^2\text{O}, 2\text{HgCl}$ , described by Bunsen (ix, 324).

*Chlorobibromide of Cacodyl*,  $\text{C}^2\text{H}^3\text{AsClBr}^2$ . — Produced by the action of bromine on protochloride of cacodyl dissolved in bisulphide of carbon, and separates as a yellow crystalline body, which is very easily resolved into bromide of methyl and a liquid which appears to be a mixture of a chlorine and a bromine compound. (Baeyer.)

*Oxide of Cacodyl*. — When potash-ley is added to protochloride of cacodyl immersed in water, a considerable rise of temperature takes place, chloride of potassium is separated, and on distilling the liquid, oxide of cacodyl passes over with the aqueous vapour. As thus obtained, it is a colourless, very mobile liquid, which has an intolerable odour, and attacks the eyes strongly, but does not fume in the air. It agrees indeed, in all its properties with the compound described by Bunsen, as paracacodylic oxide (ix, 326), which is probably the true oxide of cacodyl, while alkarsin is a mixture of the oxide with free cacodyl, to which its owes its spontaneous inflammability. (Compare Gerhardt, *Traité* I, 627.)

### Arsenmethyl. $\text{C}^3\text{H}^3\text{As}$

BAEYER. *Ann. Pharm.* 107, 279.

#### *Arsenmonomethyl, Methylarsine.*

The formation of the bichloride of this radical has been already mentioned. The radical itself has not been isolated, but a tetrachloride, an iodide, two oxygen-compounds, and a sulphide have been obtained.

*Binoxide of Arsenmethyl*.  $\text{AsC}^3\text{H}^3\text{O}^2$ . — Obtained by decomposing the bichloride, under water, with excess of carbonate of potash; extracting the mass with absolute alcohol; distilling off the alcohol by the heat of the water-bath in a stream of carbonic acid; extracting the residue (an oily liquid which soon solidifies) in a retort with bisulphide of carbon,

which leaves chloride of potassium and impurities undissolved; and leaving the solution to crystallize by spontaneous evaporation.

Large cubical but not regularly formed crystals, which have a very high specific gravity and a powerful odour like that of assafœtida. When taken out of the liquid, they generally become opaque and acquire the aspect of porcelain, but do not alter further by exposure to the air. They melt at  $95^{\circ}$ , are decomposed when distilled alone, but volatilise undecomposed together with the vapour of water or alcohol.

					Baeyer.
2 C.....	12	...	11.32	.....	11.59
3 H .....	3	...	2.83	.....	2.92
As .....	75	...	70.07	.....	67.70
2 O .....	16	...	15.78	.....	17.79
<hr/>					
AsC <sup>2</sup> H <sup>3</sup> O <sup>2</sup>	106	...	100.00	.....	100.00

The oxide distilled with hydrate of potash is for the most part resolved into arsenious acid and oxide of cacodyl:



By nitric acid, mercuric oxide and oxide of silver, in presence of water, it is easily converted into arsenmethylic acid. — Hydrocyanic acid does not act upon it. — From its concentrated aqueous solution, hydrochloric or hydrobromic acid throws down oily drops of bichloride or bibromide of arsenmethyl, and sulphydric acid produces a white precipitate of the bisulphide.

Oxide of arsenmethyl dissolves slowly but abundantly in cold water, very easily in hot water, also in alcohol, ether, and bisulphide of carbon. (Baeyer.)

*Arsenmethylic Acid.*  $\text{As}(\text{C}^2\text{H}^3)\text{H}^3\text{O}^3 = \text{As}(\text{C}^2\text{H}^3)\text{O}^4, 2\text{HO}$ . — Formed by the action of mercuric oxide on the binoxide of arsenmethyl or of oxide of silver on the bichloride. — When recently precipitated oxide of silver is added to bichloride of arsenmethyl immersed in water, chloride of silver is first formed, after which the liquid assumes a violet colour and metallic silver is precipitated. — If the addition of oxide of silver be continued till it is no longer reduced (avoiding a great excess); the filtrate then mixed with excess of hydrate of baryta; carbonic acid passed into the liquid to precipitate the excess of baryta; the filtered solution evaporated to dryness over the water-bath; the residue treated with a small quantity of water; and this solution precipitated by alcohol: neutral arsenmethyrate of baryta separates out. — Another mode of preparation is to treat the aqueous solution of the binoxide with mercuric oxide, decompose the resulting mercurous salt of arsenmethylic acid with baryta-water, and proceed as above.

By exactly precipitating the baryta from the solution of this salt with sulphuric acid, evaporating the filtrate over the water-bath, and recrystallising from hot alcohol, the hydrated acid is obtained in large spear-shaped laminæ composed of needles united in deodritic groups. It is a strong acid having a pure and agreeable sour taste; it remains unaltered in dry air and decomposes carbonates.

				Baeyer.
2 C	.....	12	.... 8.57	..... 8.77
5 H	.....	5	.... 3.57	..... 3.63
As	.....	75	.... 53.57	
6 O	.....	48	.... 34.29	
<hr/>				
$\text{As}(\text{C}^2\text{H}^3)\text{H}^2\text{O}^6$	....	140	.... 100.00	

Arsenmethylic acid is very soluble in water and dissolves in absolute alcohol much more readily than cacodylic acid. — It is bibasic, the formula of its salts being  $\text{C}^2\text{H}^3\text{As}, \text{M}^2\text{O}^6$ . All the salts either crystallize or form precipitates.

It forms an *ammonia-salt*.

*Barium-salt.* — Precipitated from the dilute aqueous solution by alcohol, in colourless needles which effloresce in the air and form a coherent mass. At  $100^\circ$  they give off 25.6 p. c. (10 At. water). The anhydrous salt separates from the concentrated aqueous solution on evaporation or on addition of alcohol: by exposure to the air under alcohol (in which it is insoluble) it is converted into the hydrated salt.

				Baeyer.
<i>Anhydrous.</i>				
2 C	.....	12.0	.... 4.36	..... 4.33
3 H	.....	3.0	.... 1.09	..... 1.82
2 Ba	.....	187.2	.... 49.80	..... 48.4 to 48.9
As	.....	75.0	.... 27.31	
6 O	.....	48.0	.... 17.44	
<hr/>				
$\text{C}^2\text{H}^3\text{AsBa}^2\text{O}^6$	....	275.2	.... 100.00	

				Baeyer.
$\text{C}^2\text{H}^3\text{AsBa}^2\text{O}^6$	.....	275.2	.... 73.6	
10 HO	.....	90.0	.... 24.4	..... 25.6
<hr/>				
$\text{C}^2\text{H}^3\text{AsBa}^2\text{O}^6 + 10\text{Aq}$	....	365.2	.... 100.00	

In Baeyer's memoir, the quantity of water in the crystals is stated to be  $10\text{H}^2\text{O}$  (or  $20\text{HO}$ ) which is evidently erroneous. — The differences between the experimental and calculated amounts of hydrogen and barium in the anhydrous salt probably arose from partial decomposition, as the salt, when redissolved in water, yielded a turbid solution.

*Silver-salt.* — Precipitated on mixing the aqueous solutions of arsen-methylate of baryta and nitrate of silver, in small nacreous anhydrous crystals which are very little altered by exposure to air and light, bear a heat of  $100^\circ$  without decomposition, but decompose with explosion at higher temperatures.

				Baeyer.
2 C	.....	12	.... 3.39	..... 3.42
3 H	.....	3	.... 0.85	..... 0.96
2 Ag	.....	216	.... 61.02	..... 61.04
As	.....	75	.... 21.18	..... 21.06
6 O	.....	48	.... 13.56	..... 13.52
<hr/>				
$\text{C}^2\text{H}^3\text{AsAg}^2\text{O}^6$	.....	354	.... 100.00	..... 100.00

*Bisulphide of Arsenmethyl.*  $\text{C}^2\text{H}^3\text{AsS}^2$ . — Produced by passing sulphuretted hydrogen into the bichloride immersed in water. Hydrochloric acid then dissolves in the water, and the sulphide separates as a colour-

less viscid mass which solidifies after a while. It dissolves in a mixture of alcohol and bisulphide of carbon, and crystallizes from the solution in shining laminæ or small prisms. It is permanent in the air, and smells faintly like *asafoetida*. It is insoluble in water, moderately soluble in alcohol, either anhydrous or anhydrated, and in ether; dissolves very readily in bisulphide of carbon, and generally separates from this solution on evaporation in oily drops which solidify after some time or immediately when touched. The crystals melt at  $110^{\circ}$ , into a mass which remains fluid long after cooling; at a higher temperature, it decomposes, with formation of sulphide of arsenic. — The alcoholic solution is decomposed by the salts of silver, copper, lead, platinum and by mercurous salts, with formation of metallic sulphides. With mercuric chloride it forms a white cloud.

					Baeyer.		
2 C.....	12	...	9.84	.....	9.99		
3 H .....	3	...	2.46	.....	2.57		
As .....	75	...	61.47	.....	64.3	...	61.7
2 S .....	32	...	26.23	.....	27.4	...	26.8
<hr/>							
C <sup>2</sup> H <sup>3</sup> AsS <sup>2</sup> .....	122	...	100.00				

*Biniiodide of Arsenmethyl.*  $C^2H^3AsI^2$ . — Produced as a yellow precipitate on adding hydriodic acid in excess to the alcoholic solution of the binoxide. The impure solution still containing chloride of calcium obtained in the preparation of the oxide may be advantageously used for the purpose.



If a precipitate forms, more alcohol must be added till it is redissolved. On leaving the solution to evaporate, the iodide separates in long shining yellow needles, which are inodorous and change but slowly on exposure to the air. They melt at about  $15^{\circ}$ , and volatilize without decomposition at  $260^{\circ}$ .

*Bichloride of Arsenmethyl.*  $C^2H^3AsCl^2$ . — Produced: 1. By the decomposition of terchloride of cacodyl between  $40^{\circ}$  and  $50^{\circ}$  (p. 494). — 2. As the ultimate product (basic perchloride of cacodyl being the first) of the action of hydrochloric acid on cacodylic acid, chloride of methyl being formed at the same time:



It may be purified if necessary, from hydrochloric acid by means of lime; then dried over chloride of calcium and distilled. — 3. It is also produced, though in a smaller quantity, by the distillation of basic perchloride of cacodyl. The substance named by Bunsen, *cacodylate of cacodylic chloride* (ix, 346) is, according to Baeyer, a mixture of bichloride of arsenmethyl with oxide of cacodyl, which latter may be kept back in the distillation of the basic perchloride of cacodyl by addition of anhydrous phosphoric acid.

Colourless, heavy, mobile, strongly refracting liquid, which boils at  $133^{\circ}$ , and does not fume in the air. Its vapour, even in the cold, exerts an intensely violent and painful action on the mucous membrane of the air-passages. It dissolves pretty readily in water, and the solution forms with sulphuretted hydrogen a white precipitate of the bisulphide.

						Baeyer.	
2 C .....	12	...	7.45	.....	7.28		
3 H .....	3	...	1.86	.....	1.93		
As .....	75	...	46.60				
2 Cl .....	71	...	44.09	.....	42.8	...	44.06
<hr/>							
C <sup>2</sup> H <sup>3</sup> AsCl <sup>3</sup>	161	...	100.00				

*Tetrachloride of Arsenmethyl.* C<sup>2</sup>H<sup>3</sup>AsCl<sup>4</sup>. — Obtained by passing chlorine into a mixture of bichloride of arsenmethyl and bisulphide of carbon cooled to 10°. — Large crystals which are very unstable, being resolved even at 0° into chloride of methyl and terchloride of arsenic.

Page 79.

### Stibethyl-compounds.

A: STRECKER. *Ann. Pharm.* 105, 396.

The analyses of the stibethyl compounds originally made by Löwig & Schweizer led to the formulæ SbEt<sup>3</sup>I<sup>2</sup>, SbEt<sup>3</sup>Cl<sup>2</sup>, &c. — W. Merck, on the other hand (x, 523) concluded from his own analyses, that these compounds contain 1 At. H more than was assigned to them by Löwig & Schweizer, and that their true formulæ are SbEt<sup>3</sup>I, HI, SbEt<sup>3</sup>Cl, HCl, &c. Merck moreover obtained, by the action of stibethyl or of ammonia on Löwig's iodide of stibethyl, a compound crystallizing in octohedrons, to which he assigned the formula SbEt<sup>3</sup>I; and from this he prepared a series of compounds, SbEt<sup>3</sup>O, SbEt<sup>3</sup>Cl, &c.; and lastly found that this compound was converted into the oxide of stibethyl by the action, not of iodine, but of hydriodic acid.

The question has more recently been taken up by Strecker, whose experiments confirm the view originally taken by Löwig and Schweizer, and show that the octohedral compound obtained by Merck is not an iodide, but an *oxyiodide*, SbEt<sup>3</sup>IO.

In proof of this view, Strecker has shown that the compound is formed by the direct union of 1 At. iodide of stibethyl with 1 At. oxide of stibethyl.



To prepare the oxyiodide in this manner, an alcoholic solution of iodide of stibethyl was divided into two equal parts; the iodine was precipitated from one of them by oxide of silver; and the filtered liquid mixed with the other; the solution then yielded by evaporation octohedral crystals of the oxyiodide. Its formation by the action of ammonia on iodide of stibethyl, observed by Merck, is represented by the equation:



The formation of the same compound by the action of stibethyl on iodide of stibethyl is attributed by Strecker to the gradual absorption of oxygen during the preparation. The analyses of the octohedral

crystals, both by Strecker and by Merck, agree very nearly with the formula  $\text{SbEt}^3\text{IO}$ , when the recently determined atomic weight of antimony is used:

					Merck.	Strecker.
Sb	.....	120	....	35.1		
12 C	.....	72	....	21.0	.....	20.65
15 H	.....	15	....	4.4	.....	4.51
I	.....	127	....	37.1	.....	36.8 .... 37.7 .... 36.9
O	.....	8	....	2.3		
<hr/>						
$\text{Sb}(\text{C}^4\text{H}^5)^3\text{IO}$	....	342	....	100.0		

Strecker considers it also possible that the oxyiodide may be formed from a mixture of stibethyl and iodide of stibethyl, without absorption of oxygen, if the mixture contains moisture; and in that case Merck's compound,  $\text{SbEt}^3\text{HI}$ , will also be produced, according to the equation:



Merck obtained indeed from such a mixture, after the octohedral crystals had separated, other crystals of greater solubility, which gave by analysis 36.5 to 36.8 p. c. iodine, and to which he assigned the formula  $\text{SbEt}^3\text{HI}$ , requiring 37.9 p. c. iodine: they were more probably  $\text{SbEt}^3\text{HI} + \text{HO}$ , which requires 36.8 p. c. iodine.

The formulæ of the other salts described by Merck may be altered in a similar manner. The *sulphate* ( $\text{SbEt}^3\text{O}, \text{SO}^3$ , according to Merck) is, according to Strecker,  $\text{SbEt}^3\text{O}^2, \text{HO}, \text{SO}^3$ , this formula requiring 14.7 p. c.  $\text{SO}^3$ ; Merck's analysis gave 14.8. — The formula of the *nitrate* ( $\text{SbEt}^3\text{O}, \text{NO}^3$ ) will in like manner be altered to  $\text{SbEt}^3\text{O}^2, \text{HO}, \text{NO}^3$ , which requires 18.9 p. c.  $\text{NO}^3$ ; analysis gave 19.0 p. c. — Merck's chloride of stibtriethyl ( $\text{SbEt}^3\text{Cl}$ ) is also an oxychloride  $\text{SbEt}^3\text{ClO}$ .

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Page 85.

### Stibmethylethylum. $(\text{C}^3\text{H}^3)(\text{C}^4\text{H}^5)^2\text{Sb}$ .

S. FRIEDLÄNDER. *J. pr. Chem.* 70, 449.

Not known in the separate state. Landolt, in 1850, obtained the iodide by the action of iodide of methyl on stibethyl. This and the other compounds of stibmethylethylum have been fully examined by Friedländer.

*Oxide*,  $\text{Sb}(\text{MeEt}^3)\text{O}$ . — Produced: 1. By decomposing the iodide with oxide of silver; when thus prepared however, it always contains silver. — 2. By decomposing the solution of the sulphate with an exactly equivalent quantity of hydrate of baryta, and concentrating the filtrate in vacuo. It is thus obtained as a thick, oily, non-volatile, somewhat yellowish liquid, which dissolves readily in water and alcohol, has an intensely bitter taste and strong alkaline reaction, expels ammonia from its salts, and precipitates many metallic oxides from their solutions, but does not decompose lime or baryta-salts. Alumina and oxide of zinc dissolve in excess of it; the oxides of manganese, iron, copper and silver are insoluble.



Oxide of stibmethylethylum unites with all oxygen-acids, forming neutral and acid salts, which may be prepared either by direct combination, or by double decomposition; it does not form basic salts. The salts are all more or less soluble in water and in alcohol; some deliquesce in the air; others are permanent. Those which crystallize do not contain any water of crystallization.

*Carbonate.* Obtained by agitating a hot solution of the sulphate with carbonate of baryta. On evaporating the filtrate, it remains as a white resinous mass, which behaves just like carbonate of ammonia.

					Friedlander.
Sb(MeEt <sup>3</sup> )O	.....	230	....	91.27	
CO <sup>2</sup>	.....	22	....	8.73	..... 8.66
<hr/>					
Sb(MeEt <sup>3</sup> )O.CO <sup>2</sup>	....	252	....	100.00	

*Sulphide* Sb(MeEt<sup>3</sup>)S. — By saturating the solution of the oxide with sulphuretted hydrogen, and evaporating out of contact with the air, the sulphide is obtained as an oily mass, which dissolves readily in water and alcohol, smells strongly of sulphuretted hydrogen, and acts on metallic salts like sulphide of ammonium.

*Sulphate.* — Produced, either by direct combination, or by decomposing the solution of the iodide with sulphate of silver. On evaporating the solution in vacuo, the salt remains in white, shining, bitter crystals, which melt at 100°, and are extremely deliquescent.

					Friedländer.
Sb(MeEt <sup>3</sup> )O	.....	230	....	85.19	
SO <sup>3</sup>	.....	40	....	14.81	..... 14.4 to 14.8
<hr/>					
Sb(MeEt <sup>3</sup> )O.SO <sup>3</sup>	.....	270	....	100.00	

*Iodide*, Sb(MeEt<sup>3</sup>)I. — Produced by the action of iodide of methyl on stibethyl. Iodide of methyl is gradually added to stibethyl (free from iodide of ethyl) and water, contained in a flask filled with carbonic acid gas; and the mixture is heated in lukewarm water, whereupon it becomes turbid, but clear again on agitation. The addition of iodide of methyl is continued till the odour of stibethyl disappears, after which the aqueous solution is separated from the excess of iodide of methyl, and slowly evaporated over the water-bath till it crystallizes.

Beautiful crystals, apparently consisting of rhombic prisms; when fresh, they have a glassy lustre, changing after a while to that of mother-of-pearl; when dry, they easily crumble to pieces, but are otherwise permanent in the air. Inodorous when cold, but at 100°, they give off a peculiar odour, without sensible decomposition; taste intensely bitter. Easily soluble in water (in twice its weight, at 20°), and in alcohol, insoluble in ether. The solutions turn the plane of polarization to the left.

							Friedländer.
Sb	.....	120	....	34.38	.....	32.98	to 33.50
14 C	.....	14	....	24.07	.....	23.03	„ 23.84
18 H	....	18	....	5.16	.....	5.57	.... 5.38
I	.....	127	....	36.39	.....	35.99	.... 36.20
<hr/>							
Sb(MeEt <sup>3</sup> )I	.....	349	....	100.00			



*Iodide of Stibmethylethylum and Mercury.* — *a.*  $\text{Sb}(\text{MeEt}^3)\text{I}$ , 2  $\text{HgI}$ . — Produced by adding recently precipitated mercuric iodide to a solution of iodide of stibmethylethylum, as long as the red colour is destroyed.

<i>Forms rhombic crystals.</i>				<i>Friedländer.</i>			
$\text{Sb}(\text{MeEt}^3)$	222	...	27.65				
2 $\text{Hg}$	200	...	24.91	.....	25.42	...	25.29
3 $\text{I}$	381	...	47.44	.....	46.39	...	46.92
<hr/>							
$\text{Sb}(\text{MeEt}^3)\text{I}, 2\text{HgI}$	803	...	100.00				

*b.*  $\text{Sb}(\text{MeEt}^3)\text{I}$ , 3  $\text{HgI}$ . — When a hot solution of mercuric chloride is added to a boiling solution of iodide of stibmethylethylum, a yellowish white precipitate is formed, which melts to an oily liquid when further heated, and solidifies in a light yellow mass on cooling. The supernatant liquid contains chloride of stibmethylethylum:



The double iodide is insoluble in water, sparingly soluble in alcohol and ether, and crystallizes from the alcoholic solution in yellow needles, which melt below  $100^\circ$ .

				<i>Friedländer.</i>			
$\text{Sb}(\text{MeEt}^3)$	222	...	21.56				
3 $\text{Hg}$	300	...	29.12	.....	28.68	...	28.59
4 $\text{I}$	508	...	49.32	.....	50.15	...	48.65
<hr/>							
$\text{Sb}(\text{MeEt}^3)\text{I}, 3\text{HI}$	1030	...	100.00				

*Chloride of Stibmethylethylum.* — Obtained by the action of hydrochloric acid on the oxide or carbonate, or, as abovementioned, by adding 2 At. mercuric chloride to 3 At. iodide of mercury, in hot solutions, and evaporating the liquid after separating it from drops of oil.

Small crystalline needles permanent in the air.

				<i>Friedländer.</i>			
$\text{Sb}(\text{MeEt}^3)$	222.0	...	86.21				
$\text{Cl}$	35.5	...	13.79	.....	13.69		
<hr/>							
$\text{Sb}(\text{MeEt}^3)\text{Cl}$	257.5	...	100.00				

*Cyanide.* — Hydrocyanic acid added to a solution of the oxide, forms a clear watery liquid which, in the dilute state, gives off hydrocyanic acid when treated with hydrochloric acid, but when concentrated, forms with that acid, a thick white precipitate insoluble in water. — Boiled with potash-ley, it gives off ammonia and forms an antimonietted acid, which yields insoluble or sparingly soluble salts with all bases, excepting potash, soda and ammonia.

*Formiate.* — Obtained by mixing hot solutions of formiate of lead and iodide of stibmethylethylum in equivalent proportions, and filtering hot. The solution, if not too dilute, deposits on cooling, interlaced silky needles, which are permanent in the air and exhibit but very faintly the characteristic odour of stibethyl-compounds. They acquire a yellowish colour by long exposure to light, but retain their silky lustre when kept

in the dark. Heated on platinum foil, they burn with a faint flame. — They are very sparingly soluble in cold water or alcohol, but boiling water dissolves a considerable quantity.

Friedländer.				
Sb.....	120	....	44.95	
16 C .....	96	....	35.95	..... 35.81
19 H .....	19	....	7.12	..... 7.34
4 O .....	32	....	11.98	
<hr/>				
Sb(MeEt <sup>3</sup> ),C <sup>2</sup> HO <sup>4</sup> .....	267	....	100.00	

*Acetate.* Sb(MeEt<sup>3</sup>),C<sup>4</sup>H<sup>3</sup>O<sup>4</sup>.! — Obtained by decomposing the sulphate with acetate of baryta. Anhydrous needles, which deliquesce slowly in the air, and dissolve readily in water.

*Butyrate.* Sb(MeEt<sup>3</sup>),C<sup>8</sup>H<sup>7</sup>O<sup>4</sup>. — Prepared like the acetate. On evaporating the aqueous solution, it remains in the form of a white, anhydrous, crystalline, non-deliquescent mass, which melts at 100°.

*Oxalate.* — *a. Neutral.* — When crystallized oxalic acid is added to a solution of oxide of stibmethylethylum, in the proportion of 1 At. of the acid (C<sup>4</sup>H<sup>2</sup>O<sup>8</sup>) to 2 At. of the oxide, the neutral salt is obtained in anhydrous needles, having a glassy lustre, and moderately soluble in water.

Friedländer.				
2Sb(MeEt <sup>3</sup> )O .....	460	....	86.47	
C <sup>4</sup> O <sup>8</sup> .....	72	....	13.53	..... 13.49
<hr/>				
C <sup>4</sup> (SbMeEt <sup>3</sup> ) <sup>2</sup> O <sup>8</sup> .....	532	....	100.00	

*b. Acid.* C<sup>4</sup>(SbMeEt<sup>3</sup>)<sup>3</sup>HO<sup>8</sup>. — Obtained by adding 1 At. oxalic acid to a solution of 1 At. of the oxide. Crystallizes by evaporation in beautiful needles, having a glassy lustre, and very soluble in water.

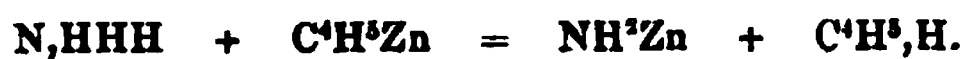
*Tartrate.* A solution of 2 At. oxide of stibmethylethylum and 1 At. tartaric acid (C<sup>8</sup>H<sup>4</sup>O<sup>10</sup>), cannot be made to crystallize, but leaves on evaporation, a syrupy liquid which absorbs water with avidity.

Page 90.

## Zincethyl.

FRANKLAND. *Proc. Roy. Soc.* 8, 502 ; *Phil. Mag.* [4] 15, 149.

*Action of Zinc-ethyl on Ammonia.* — Dry ammonia-gas passed through an ethereal solution of zinc-ethyl, is rapidly absorbed; an abundant evolution of hydride of ethyl soon begins; and after a little while, zinc-amide NH<sup>2</sup>Zn separates out :



Zinc-amide is a white amorphous body, insoluble in ether. It is instantly decomposed by water and by alcohol, with evolution of great heat, and regeneration of ammonia :



Heated with iodide of ethyl in a sealed tube to  $145^\circ$ , it forms iodide of zinc and iodide of biethylammonium :



Zinc-amide may be heated to  $200^\circ$  without decomposition ; but at a dull red heat, it is resolved into ammonia and zinc-nitride  $\text{NZn}^2$ .



Zinc-nitride is a grey powder, which may be heated out of contact of air, without melting, decomposing, or volatilizing; but is decomposed with great violence by water :



If merely moistened with water, it becomes red hot.

*Zinc-phenylimide.*  $\text{N},\text{C}^{12}\text{H}^5,\text{H},\text{Zn}$ . — Zincethyl acts with great violence on anhydrous phenylamine (aniline). A more moderate action is obtained by adding the phenylamine to an ethereal solution of zinc-ethyl, and in that case, hydride of ethyl is evolved, and the liquid ultimately concretes into a semi-fluid mass consisting of zinc-phenylimide.



In contact with water, zinc-phenylimide reproduces phenylamine.

*Biethylzincamine*,  $\text{N}(\text{C}^4\text{H}^5)^2\text{Zn}$ , is produced in like manner by the action of zincethyl on biethylamine :



Its reactions are similar to the preceding.

*Zinc-oximide.*  $\text{N}^2(\text{C}^4\text{O}^4)'\text{H}^2,\text{Zn}^2$ . — Pure zinc-ethyl does not act upon dry oxamide at ordinary temperatures ; but at  $100^\circ$ , a violent action takes place, attended with evolution of hydride of ethyl and formation of zinc-oximide, which remains combined with zinc-ethyl.



Oxamide.

*Zinc-acetamide.*  $\text{N},\text{C}^4\text{H}^3\text{O}^2,\text{HZn}$ . — Zincethyl acts violently on acetamide, hydride of ethyl being evolved, and zinc-acetamide formed, as a white amorphous powder which, in contact with water, reproduces acetamide.

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Page 96.

## Stannethyls.

STRECKER. *Ann. Pharm.* 105, 310.

The formulæ of the numerous compounds of tin and ethyl, distinguished by Löwig, may, according to Strecker, be reduced to two or three simple types, by a modification similar to that proposed for the stibethyl-compounds (p. 499) viz., by regarding Löwig's iodides, chlorides, &c., as oxyiodides, oxychlorides, &c. Thus: Löwig's *iodide of methylene-stannethyl*,  $\text{Sn}^2(\text{C}^4\text{H}^5)^2\text{I}$ , gave by analysis 15.1 and 14.8 p. c. carbon, 3.3 and 3.1 hydrogen, and 41.2 iodine, which numbers agree with the formula  $\text{Sn}^2(\text{C}^4\text{H}^5)^2\text{IO}$  (15.5 C, 3.2 H, and 41.2 I), better than with Löwig's formula (15.9 C, 3.3 H, and 41.7 I). Moreover, Löwig himself, states that the oxide precipitated from this iodide by ammonia, is not distinguishable from oxide of stannethyl  $\text{Sn}(\text{C}^4\text{H}^5)\text{O}$ . Now, the oxide precipitated from the compound  $\text{Sn}^2(\text{C}^4\text{H}^5)^2\text{IO}$ , would actually be  $\text{Sn}^2(\text{C}^4\text{H}^5)^2\text{O}^2$ , or  $\text{Sn}(\text{C}^4\text{H}^5)\text{O}$ , whereas that derived from the iodide  $\text{Sn}^2(\text{C}^4\text{H}^5)^2\text{I}$ , would have a different composition, viz.,  $\text{Sn}^2(\text{C}^4\text{H}^5)^2\text{O}$ .

Löwig's *iodide of ethylene-stannethyl*  $\text{Sn}^4(\text{C}^4\text{H}^5)^4\text{I}$ , appears also to be an oxyiodide  $\text{Sn}^4(\text{C}^4\text{H}^5)^4\text{IO}^2$ , the corresponding oxide likewise agreeing in all essential particulars with oxide of stannethyl.

	$\text{Sn}^4(\text{C}^4\text{H}^5)^4\text{IO}^2$ .		Analysis (Löwig).		$\text{Sn}^4(\text{C}^4\text{H}^5)^4\text{I}$ .	
C .....	19.2	.....	19.1	to 19.7	.....	20.08
H .....	4.0	.....	4.2	„ 4.5	.....	4.18
I .....	25.4	.....	25.1	„ 26.5	.....	26.36

According to Strecker's view, the radicals *methylene-stannethyl* and *ethylene-stannethyl* are identical with stannethyl; so likewise are their oxides; and in the iodine-compounds, the sum of the equivalents of oxygen and iodine is constant, viz.,  $\text{SnEtI}$  or  $\text{Sn}^4\text{Et}^4\text{I}^4$ ;  $\text{Sn}^3\text{Et}^3\text{IO}$ , or  $\text{Sn}^4\text{Et}^4\text{I}^2\text{O}^2$ , and  $\text{Sn}^4\text{Et}^4\text{IO}^2$ .

The compounds of *ethylostannethyl*  $\text{Sn}^4(\text{C}^4\text{H}^5)^6$  (ix, 104), may be regarded as double compounds, containing stannethyl and methylostannethyl [ $\text{Sn}^4\text{Et}^6 = 2\text{SnEt} + \text{Sn}^2\text{Et}^3$ ], the iodide, chloride, &c., being also supposed to contain oxygen.

Lastly, the compounds of *acetostannethyl*  $\text{Sn}^4(\text{C}^4\text{H}^5)^3$  (ix, 101), may be represented as double compounds containing stannethyl and bistannethyl [ $\text{Sn}^4\text{Et}^3 = 2\text{SnEt} + \text{Sn}^2\text{Et}$ ]. Thus Löwig's iodide of acetostannethyl  $\text{Sn}^4\text{Et}^3\text{I}$ , may be regarded as an *oxyiodide*, containing  $2\text{SnEtO} + \text{Sn}^2\text{EtI}$ ,

$2\text{Sn}(\text{C}^4\text{H}^5)\text{O}, \text{Sn}^2(\text{C}^4\text{H}^5)\text{I}.$				Analysis.				$\text{Sn}^4(\text{C}^4\text{H}^5)^3\text{I}.$	
Sn	....	50.2	.....	....	51.6	....	.....	52.6	
C	....	15.6	.....	15.3	....	....	15.5	.....	16.0
H	....	3.2	.....	3.4	....	....	3.6	.....	3.3
I	....	27.5	.....	28.1	....	....	28.6	.....	28.0
O	....	3.5							

On the same hypothesis, the corresponding nitrate, which gave by analysis 18.3 p. c. C, 4.7 H, and 13.7  $\text{NO}^5$ , may be represented by the formula  $2\text{Sn}(\text{C}^4\text{H}^5)\text{O} + \text{Sn}^2(\text{C}^4\text{H}^5)\text{O}, \text{NO}^5$ , which requires 18.1 C, 3.8 H, and 13.6  $\text{NO}^5$ , while Löwig's formula  $\text{Sn}^4(\text{C}^4\text{H}^5)^3\text{O}, \text{NO}^5$ , requires 18.7 C, 3.9 H, and 14.0  $\text{NO}^5$ .

If these views are correct, the number of distinct radicals contained in Löwig's compounds must be reduced to three, viz., *bistannethyl*  $\text{Sn}^2(\text{C}^4\text{H}^5)$ , *stannethyl*  $\text{Sn}(\text{C}^4\text{H}^5)$ , or  $\text{Sn}^2(\text{C}^4\text{H}^5)^2$ , and *bistannic triethyl* or *methylo-stannethyl*  $\text{Sn}^2(\text{C}^4\text{H}^5)^3$ .

### Stannic Biethyl. $\text{Sn}(\text{C}^4\text{H}^5)^2$ .

FRANKLAND. *Ann. Pharm.* 111, 44; abstr. *Proc. Roy. Soc.* 9, 672.

BUCKTON. *Phil. Trans.* 1859, 424; abstr. *Proc. Roy. Soc.* 9, 309, 686.

*Stannic Ethide.* (Frankland.)

Produced by the action of zinc-ethyl on iodide of stannethyl:



Crystallized iodide of stannethyl gradually added to a strong ethereal solution of zinc-ethyl, dissolves with considerable evolution of heat, and then becomes syrupy; to ensure the complete decomposition of the iodide, the zinc-ethyl must be added in slight excess. On distilling the syrupy liquid, the thermometer quickly rises to  $180^\circ$ , and the greater part of the product, consisting of stannic biethyl, together with excess of zinc-ethyl, passes over between  $180^\circ$  and  $200^\circ$ . The distillate is washed with water to decompose the zinc-ethyl; the separated oxide of zinc is dissolved by acetic acid; and the heavy ethereal liquid is separated from the watery layer, dried by contact with chloride of calcium, and then rectified. (Frankland). — Buckton washes the crude product with water and acid before distilling, and finds that the greater portion then passes over between  $170^\circ$  and  $180^\circ$ .

*Properties.* Transparent colourless liquid, having a very faint ethereal odour, like that of oxide of stannethyl, and a somewhat metallic but not unpleasant taste. Sp. gr. 1.187 at  $23^\circ$  (Frankland); 1.192 (Buckton). Boils at  $181^\circ$ , and distils without decomposition. Vapour-density 8.021. (Frankland.)

				Frankland.	Buckton.
Sn .....	59	...	50.43	50.28	
8 C .....	48	...	41.02	41.01	40.56
10 H .....	10	...	8.55	8.48	8.62
$\text{Sn}(\text{C}^4\text{H}^5)^2$ .....	117	...	100.00	99.77	

	Vol.	Density.		Vol.	Density.
Sn-vapour .....	1	4.0905	Or: Tin-vapour .....	1	4.0905
C-vapour .....	8	3.3280	Ethyl-vapour .....	2	4.0210
H-gas .....	10	0.6930			
Vap. of $\text{Sn}(\text{C}^4\text{H}^5)^2$	1	8.1115		1	8.1115

Stannic biethyl is inflammable, and burns with a lurid flame with blue edges, giving off a thick white cloud of stannic oxide. In oxygen

gas, it burns with greater brilliancy, producing a white flame edged with blue. — It does not unite directly with iodine, bromine, and chlorine, &c., but is decomposed into ethyl and stannethyl, both of which unite with the iodine, bromine, &c. (Frankland, Buckton.) — It does not decompose water; neither is it acted upon by concentrated acids at ordinary temperatures; but on heating the mixture, gases are given off and salts are formed, differing in constitution according to the duration of the action. (Frankland, Buckton.) Heated to 80° or 90° with concentrated hydrochloric acid, it gives off hydride of ethyl and forms chloride of bistannic triethyl:



According to this equation, stannic biethyl should give off 12.39 p. c. of ethyl in the form of hydride: by experiment it was found to yield 11.55 p. c. (Frankland.)

Stannic biethyl is nearly insoluble in water, and sparingly soluble in alcohol; but ether takes it up freely. (Buckton.)

### Bistannic Triethyl. $\text{Sn}^2(\text{C}^4\text{H}^5)^3$ .

BUCKTON. *Phil. Trans.* 1859, 426.

CAHOURE. *Compt. rend.* 48, 833; *Ann. Pharm.* 111, 236.

#### *Sesquistannethyl, Methylostannethyl.*

Obtained in the free state, together with stannethyl, by heating iodide of ethyl to 140° or 150°, in a sealed tube, with an alloy of 4 to 6 pts. tin and 1 pt. sodium. The two radicals may be separated by alcohol, in which stannethyl dissolves with great facility. (Cahours.) — Bistannic triethyl is also formed as an iodide, when iodide of ethyl is heated with an alloy of 1 pt. sodium and 8, 10, or 12 pts. tin. (Cahours.)



and as a chloride, by the action of bichloride of tin on stannic biethyl,—or again, by the action of bichloride of tin on a quantity of zinc-ethyl not quite sufficient to remove all the chlorine. (Buckton.)



If on the other hand the zinc-ethyl is in excess, the radical stannic biethyl is formed:



and if 1 At. of the bichloride is used to 1 At. zinc-ethyl, an impure chloride of stannethyl is obtained.



Bistannic triethyl in the free state is a very mobile liquid, which volatilizes without decomposition, and combines directly with oxygen, chlorine, bromine, and iodine.

*Oxide of Bistannic Triethyl*, obtained by decomposing the chloride, iodide, or any of the salts with potash, is an oily liquid, which is heavier than water, has a powerful odour and caustic taste, and produces painful blisters when left in contact with the skin. It volatilizes without decomposition. It is moderately soluble in water, and neutralizes acids completely, forming crystallizable salts. (Cahours, Buckton.)

The *sulphate*, obtained by neutralizing the aqueous solution of the oxide with sulphuric acid and heating the liquid to 80°, is opaque, colourless, and crystallizes in needles or grains, which under the microscope, appear as well defined octohedrons. It is very volatile, and attacks the nose vigorously. It is inflammable, by which property, as well as by its crystalline form, it is distinguished from sulphate of stannethyl, which crystallizes in small roundish irregular plates. It is much more soluble in cold than in hot water, a clear cold saturated solution becoming semisolid when heated near the boiling point. (Buckton.)

					Buckton.
2 Sn.....	118	...	46.64		
12 C .....	72	...	28.45	.....	28.02
15 H .....	15	...	5.92	.....	5.91
S .....	16	...	6.33	.....	6.41
4 O .....	32	...	12.66		
<hr/> Sn <sup>2</sup> (C <sup>4</sup> H <sup>5</sup> ) <sup>3</sup> ,SO <sup>4</sup> .....					
	253	...	100.00		

*Iodide of Bistannic Triethyl*. Sn<sup>2</sup>(C<sup>4</sup>H<sup>5</sup>)<sup>3</sup>I. — Produced: 1. By gradually adding iodine to bistannic triethyl, care being taken to keep the liquid cool. If the iodine is quickly added, and the liquid allowed to become hot, the products formed are iodide of stannethyl and iodide of ethyl:



— 2. By heating iodide of ethyl with an alloy of 1 pt. sodium and 8, 10, or 12 pts. tin. (Cahours.)

Volatile liquid, having a very strong odour of mustard, and exciting tears. Sp. gr. 1.833 at 15°; boiling point 208° to 210°.

Treated with excess of iodine, it is converted into iodide of ethyl and iodide of stannethyl, which separates in beautiful prisms;



With soluble silver-salts, it yields iodide of silver and a compound of bistannic triethyl with the corresponding acid. (Cahours.)

The *bromide* is obtained in like manner by the direct action of bromine on the radical. (Cahours.)

*Chloride of Bistannic Triethyl*. Sn<sup>2</sup>(C<sup>4</sup>H<sup>5</sup>)<sup>3</sup>Cl, is obtained: 1. By the action of bichloride of tin on zinc-ethyl (p. 507). — 2. By the action of bichloride of tin on stannic biethyl, in the proportion of 3 pts. of the former to 4 of the latter. The mixture became hot, and when distilled, began to boil at about 200°, the thermometer slowly rising to 220°, at which temperature the whole had passed over, leaving only a trace of solid matter. The portion which distilled below 210° was oily, but that which passed above 210°, solidified on cooling into a mass of crystals, which gave by analysis 24.49 p. c. carbon, 4.84 hydrogen, and 24.20

chlorine, agreeing approximately with the formula of a *double chloride of stannethyl and bistannic triethyl*,  $5\text{SnC}^4\text{H}^6\text{Cl}$ , +  $\text{Sn}^3(\text{C}^4\text{H}^6)^3\text{Cl}$ , which requires 22.37 p. c. C, 4.66 H, and 24.82 Cl.

The oily liquid which passed over below  $210^\circ$ , appeared to be a mixture of chloride of bistannic triethyl with the double chloride just mentioned. Treated with caustic potash-ley, it yielded a precipitate of oxide of stannethyl and an alkaline solution, from which hydrochloric acid separated the oxide of bistannic triethyl. (Buckton.)

Anhydrous *protochloride of tin* added in powder to zinc-ethyl, appears to yield a compound of stannethyl with chloride of zinc; and on distilling the product, the greater part of the stannethyl is resolved into metallic tin and stannic biethyl. (Buckton.)

Zinc-methyl acts with tin and the alloys of tin in the same manner as zinc-ethyl, yielding the radicals  $\text{SnC}^3\text{H}^3$  and  $\text{Sn}^2(\text{C}^3\text{H}^3)^2$ . (Cahours.)

Stannic Ethylomethyl.  $\text{Sn}(\text{C}^3\text{H}^3)(\text{C}^4\text{H}^6)$ .

FRANKLAND. *Ann. Pharm.* 111, 50.

*Stannic Ethylomethide.*

Produced by the action of zinc-methyl on iodide of stannethyl. On adding about 3 oz. of crystallized iodide of stannethyl to zinc-methyl dissolved in ether, considerable heat was evolved, rendering it necessary to immerse the vessel in cold water. On treating the product in the manner described for the preparation of stannic biethyl (p 506.), stannic ethylomethyl passed over between  $143^\circ$  and  $148^\circ$ .

Transparent colourless liquid, having a very faint ethereal odour and slightly metallic taste. Sp. gr. 1.2319 at  $19^\circ$ . Does not solidify at  $13^\circ$ . Boils between  $144^\circ$  and  $146^\circ$ . Vapour-density 6.838.

Sn .....	59	...	57.28	.....	57.44
6 C .....	36	...	34.95	.....	35.09
8 H .....	8	...	7.77	.....	7.98

SnMeEt .....	103	...	100.00	.....	100.51
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	Vol.	Density.			Vol.	Density.
Sn-vapour .....	1	4.0905	or :	Tin-vapour .....	1	4.0905
C-vapour .....	6	2.4960		Methyl-vapour	1	2.0105
H-gas....	8	0.5544		Ethyl-vapour ....	1	1.0399
<hr/>						
Vapour of SnMeEt ....	1	7.1409			1	7.1409

Stannic ethylomethyl is easily inflammable, and burns in air and in oxygen, like stannic biethyl. It also reacts like that body with chlorine, iodine, and bromine, a methyl-compound being separated in each case. Treated with hot hydrochloric acid, it is decomposed, yielding a crystal-



lizable salt, and a gaseous mixture consisting of 81·21 p. c. hydride of ethyl and 18·79 p. c. hydride of methyl.

Stannic ethylomethyl dissolves iodine, assuming a splendid crimson colour, which disappears very slowly unless heat is applied. The products of the action are iodide of methyl and diniodide of stannethyl ( $\text{SnEt}^2\text{I}$ ). (Löwig's iodide of methylene-stannethyl.)



*Diniiodide of Stannethyl* is a dark straw-coloured somewhat oily liquid, which does not solidify at  $-13^\circ$ . It has an extremely pungent and intolerable odour, resembling that of oil of mustard. Sp. gr. 2·0329 at  $15^\circ$ . Begins to boil at  $208^\circ$ , but cannot be distilled without decomposition.

					Frankland.
2 Sn .....	118	...	38·94	.....	39·07
8 C .....	48	...	15·84	.....	15·94
10 H .....	10	...	3·30	.....	3·42
I .....	127	...	41·92	.....	42·78
<hr/>					
$\text{Sn}^2(\text{C}^4\text{H}^6)^2\text{I}$ .....	303	...	100·00	.....	101·21

This is the compound to which Strecker assigns the formula,  $\text{Sn}^2\text{Et}^2\text{IO}$ : its formation in the manner just mentioned can however scarcely be reconciled with this view of its composition.

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Page 106.

### Plumbethyls.

BUCKTON. *Phil. Trans.* 1859, 430; abstr. *Proc. Roy. Soc.* 9, 312, 680.

*Plumbic Biethyl.*  $\text{C}^2\text{H}^4\text{Pb} = \text{PbEt}^2$ .— Obtained by the action of zinc-ethyl on chloride of lead:



Chloride of lead introduced into zinc-ethyl, immediately turns black, from separation of metallic lead, and forms a hard crust at the bottom of the liquid; hence it is more convenient to operate in a bottle than in a retort. The mass is incorporated by stirring; and as soon as the chloride ceases to change colour, the vessel is heated to  $100^\circ$  in a water-bath, then left to cool; and the liquid, which is a compound of the lead-radical with zinc-ethyl, is decanted, treated with very dilute hydrochloric acid, and then washed with water. The mass of chloride of zinc in the first vessel, yields an additional quantity of the radical by agitation with anhydrous ether. On attempting to purify the product by distillation, the thermometer rises quickly to above  $200^\circ$ , and decomposition then takes place, attended with deposition of metallic lead. This difficulty, may however, be obviated, by distilling the liquid under reduced pressure; under a pressure of  $7\frac{1}{2}$  inches of mercury, it distils unaltered at  $152^\circ$ .

Transparent colourless liquid, having a faint ethereal odour. Sp. gr. 1.62. Insoluble in water, soluble in ether.

					Buckton.
Pb	.....	103.5	....	64.09	
8 C	.....	48.0	....	29.72	..... 29.68
10 H	.....	10.0	....	6.19	..... 6.23
<hr/>					
Pb(C <sup>4</sup> H <sup>5</sup> ) <sup>2</sup>	.....	161.5	....	100.00	

Plumbic biethyl burns brightly, giving off copious fumes of oxide of lead. The flame has a faint green tinge, with a border less luminous than that of the flame of stannic biethyl. It acts violently on bromine and iodine, yielding, as ultimate products, bromide and iodide of lead. When poured into chlorine gas, it takes fire. With concentrated acids, it forms salts of *biplumbic triethyl* Pb<sup>2</sup>Et<sup>3</sup>, and gives off hydride of ethyl; e. g. with hydrochloric acid :



### Compounds of Biplumbic Triethyl.

**Chloride.** Pb<sup>2</sup>Et<sup>3</sup>Cl. — Prepared by passing excess of hydrochloric acid gas into a tube containing plumbic biethyl moistened with the aqueous acid. After brisk effervescence, a solid mass is formed which may be freely exposed to the air, till acid fumes cease to rise. It dissolves in ether, and may be obtained by spontaneous evaporation, in long colourless crystals, having a strong penetrating odour, like that of the corresponding tin-compound (p. 508). It melts between watch-glasses, and ignites at a comparatively low temperature with the characteristic lead-flame. Heated with strong sulphuric acid, it blackens and is converted into sulphate of lead.

					Buckton.
2 Pb	.....	207.0	....	62.85	..... 62.51
12 C	..	72.0	....	21.85	..... 21.69
15 H	.....	15.0	....	4.55	..... 4.57
Cl	.....	35.5	....	10.75	..... 11.33
<hr/>					
Pb <sup>2</sup> (C <sup>4</sup> H <sup>5</sup> ) <sup>3</sup> Cl	.....	329.5	....	100.00	..... 100.00

**Sulphate.** Pb<sup>2</sup>Et<sup>3</sup>,SO<sup>4</sup>. — Prepared by adding dilute sulphuric acid to a warm solution of the chloride. Crystallizes on cooling, in fine asbestos-like needles, which may be purified and obtained of considerable size by crystallization from alcohol.

					Buckton.
2 Pb	.....	207	....	60.53	
12 C	.....	72	....	21.05	..... 20.77
15 H	.....	15	....	4.39	..... 4.47
S	.....	16	....	4.68	
4 O	.....	32	....	9.35	
<hr/>					
Pb <sup>2</sup> (C <sup>4</sup> H <sup>5</sup> ) <sup>3</sup> SO <sup>4</sup>	.....	342	....	100.00	

*Oxide.* — Obtained by heating the chloride either with aqueous potash or with oxide of silver. It is oily while warm, but solidifies in a crystalline mass on cooling, and volatilizes at a stronger heat in white pungent vapours, which provoke sneezing. It strongly blues litmus paper, and absorbs carbonic acid from the air, forming a crystalline carbonate. The various salts of biplumbic triethyl may easily be obtained from the oxide or the carbonate.

Biplumbic triethyl is identical with Löwig's *methyloplumbethyl*, which he obtained as an iodide by acting upon iodide of ethyl with an alloy of lead and sodium. Buckton found this reaction to take place very slowly, even at the boiling point of the iodide of ethyl. — Neither bromide nor iodide of ethyl showed any tendency to unite with granulated lead when exposed to sunshine or heated under pressure to 170°, the bromide remaining quite unchanged, and the iodide yielding iodide of lead and gaseous matter. (Buckton.)

Page 109.

### Mercuric Ethyl. $C^4H^6Hg$ .

BUCKTON. *Phil. Trans.* 1859, 417; abstr. *Proc. Roy. Soc.* 9, 685.

*Formation and Preparation.* 1. By the action of zinc-ethyl on iodide of mercurous ethyl :



Dry pulverized iodide of mercurous ethyl, is added by small quantities to zinc-ethyl contained in a retort, through which a stream of coal-gas is passing, the mixture being incorporated by stirring; and, as soon as the zinc-ethyl is saturated,—which may be known by the stirring rod ceasing to fume on exposure to the—air, the product is distilled till nothing but gases pass over. The product, which is a heavy liquid mixed with a little ether, is then distilled with a slight excess of zinc-ethyl, to ensure complete decomposition of the iodide, then washed with hydrochloric acid and afterwards with water, and rectified. — 2. By heating zinc-ethyl with mercuric chloride :



An excess of mercuric chloride must be avoided, as otherwise, chloride of mercurous ethyl will be formed :



The slight excess of zinc-ethyl is decomposed by water, and the separated oxide of zinc dissolved out by dilute hydrochloric acid. This process gives a very good result; but the former is preferable, as it occasions less consumption of zinc-ethyl.

3. By the action of cyanide of potassium on the iodide of mercurous ethyl:



This mode of preparation is not advantageous, being attended with considerable loss.

*Properties.* Transparent colourless liquid, having a faint ethereal odour. It is insoluble in water, sparingly soluble in alcohol, readily in ether. Sp. gr. 2.46. Boiling point  $158^\circ$  to  $160^\circ$ . Vapour-density 9.97.

					Buckton.
Hg	.....	100	...	77.53	..... 77.24
4 C	.....	24	...	18.60	..... 18.66
5 H	.....	5	...	3.87	..... 3.72
<hr/>					
C <sup>4</sup> H <sup>5</sup> Hg	.....	129	...	100.00	..... 99.62
<hr/>					
			Vol.	Density.	
Mercury-vapour	.....	1	.....	6.9300	
Ethyl-vapour	.....	1	.....	2.0105	
<hr/>					
Vap. of C <sup>4</sup> H <sup>5</sup> Hg	.....	1	.....	8.9405	

Considerable difficulty was experienced in determining the vapour-density by experiment, the vapour being decomposed at about  $226^\circ$  into mercury and an inflammable gas, probably a mixture of ethylene and hydride of ethyl.

The formula of mercuric ethyl ought perhaps to be doubled, so as to make it represent 2 volumes of vapour. The great difference between the boiling points of mercuric methyl ( $96^\circ$ ) and mercuric ethyl ( $160^\circ$ ) is also in favour of this view. A test of its correctness was sought in the action of zinc-ethyl on iodide of mercurous methyl, which, if mercuric-ethyl be really  $\text{Hg}^2\text{Et}^2$ , might be expected to yield *mercuric ethylomethyl*

$\text{Hg}^2 \begin{Bmatrix} \text{Me} \\ \text{Et} \end{Bmatrix}$  The two substances act upon each other with evolution of heat, and a distillate is obtained, varying from  $60^\circ$  to  $160^\circ$ ; but on rectifying the product, nothing is obtained but mercuric ethyl and mercuric methyl. Possibly mercuric ethylomethyl is first formed and then decomposed by heat. (Buckton.)—Frankland obtained a similar result; also by the action of zinc-methyl on chloride of mercurous ethyl. (*Proc. Roy. Soc.* 9, 676.)

*Decompositions.* 1. Mercuric ethyl burns with a smoky flame, more luminous than that of mercurous ethyl, giving off a large quantity of mercurial vapour. — 2. When poured into chlorine gas, it bursts into flame and is almost entirely destroyed. It acts violently also with iodine or bromine, but if the action be conducted under water, ethyl or its products of decomposition are eliminated; if the liquid is kept cool by a freezing mixture, the nascent ethyl unites with the bromine:



3. With sulphuric and hydrochloric acid, it behaves like mercuric methyl (p.398), yielding hydride of ethyl and sulphate or chloride of mercurous ethyl:



4. Sodium slowly decomposes mercuric ethyl, forming a bulky grey spongy mass, which is very liable to explode from slight causes, and instantly takes fire on coming in contact with the air. On applying a

gentle heat, a violent evolution of gas takes place, consisting of ethylene and hydride of ethyl. Probably sodium-ethyl is first formed:



and then decomposed by heat:



*Action of Zinc-ethyl on the Chlorides of Silver, Copper, and Platinum.*—Zinc-ethyl acts violently on chloride of silver, the latter being partly reduced to the metallic state, and on the addition of water, effervescence takes place and chloride of zinc alone is found in solution. The action appears to be:



Similar reactions appear to take place with protochloride of platinum and subchloride of copper  $\text{Cu}^2\text{Cl}$ , no organo-metallic body being formed in either case. (Buckton.)

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Page 111.

## Oxalic Acid.

*Formation.* Alcohol may be converted into oxalic acid, by the action of bichloride of platinum. Schlossberger found (*Ann. Pharm.* 110, 247) that the ether-alcohol washings of chloroplatinate of ammonium from nitrogen-determinations, which had been accumulating for several years in his laboratory, on being mixed with water and freed from excess of platinum by sulphuretted hydrogen, yielded by evaporation fine colourless prisms of oxalic acid. The remaining acid liquid when neutralized with soda and evaporated, yielded brown syrupy residues, probably containing products of oxidation, similar to those which Debus obtained by the action of nitric acid upon alcohol.

*Sesquichloride and protochloride of carbon*, are converted into oxalic acid, when heated in a sealed tube with hydrate of potash, the former to  $210^\circ$ — $220^\circ$ , the latter to about  $200^\circ$ . With sesquichloride of carbon, the reaction is—



No other products are formed, but the quantity of the sesquichloride converted into oxalate of potash is very small in proportion to the whole.

With protochloride of carbon, the reaction is—



The proportion of oxalic acid formed in this case is much greater than in the former. (Geuther, *Ann. Pharm.* 111, 176), compare p. 421.

For the formation of oxalic acid from glycol see p. 423. — Difference of action of potash and soda in the formation of oxalic acid from starch, lignin, &c., p. 385.

*Action of Oxalic Acid on Salts.*—Oxalic acid in solution readily decomposes fluoride of calcium, eliminating hydrofluoric acid. It decomposes the phosphates of iron, silver, zinc, and copper, and the arseniates of iron, silver and copper, setting the phosphoric or arsenic acid free. It dissolves the protosulphides of iron and manganese, but not the sulphides of zinc, cadmium, uranium, cobalt, mercury, or copper. It decomposes most chromates, the liberated chromic acid likewise suffering decomposition, especially if the liquid be heated. Chromate of zinc is first dissolved with yellow colour; but after awhile, and especially if heat be applied, oxalate of zinc separates out and oxalate of chromium remains in solution. The chromates of baryta, bismuth, mercury and oxide of lead are immediately decomposed by oxalic acid, without previous solution; chromate of lead dried at a strong heat, is scarcely attacked by oxalic acid. Terchloride of antimony is decomposed by concentrated solution of oxalic acid; the precipitate is free from chlorine, and is but very slowly decomposed by boiling water. Finely pounded glass is rapidly attacked by oxalic acid, the lime and alkali being dissolved out and the silica separated. Many minerals are also decomposed by oxalic acid; its presence in lichens probably contributes to the decomposition of rocks. (J. W. Slater, *Chem. Gaz.* 1856, 120.)

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Page 127.

### Oxalates.

SOUCHAY & LENNSEN. *Ann. Pharm.* 99, 31; 100, 308; 102, 35, 41; 103, 308; 105, 245; *abst. Jahrb. d. Chem.* 1856, 446; 1857, 289; 1858, 243.

*Acid Oxalate of Soda*,  $C^4HNaO^8 + Aq$ , dissolves in 60.3 pts. of water at  $15.5^\circ$ , and in 47 pts. of boiling water; the latter solution, if left to cool quietly, sometimes remains supersaturated. It does not give off any water when left to stand over oil of vitriol; but at ordinary temperatures, it gives off its water of crystallization at  $100^\circ$ , and hydrated oxalic acid at  $160^\circ$ .

It does not appear possible to prepare oxalate of soda containing a larger proportion of oxalic acid.

*Oxalate of Lithia.* The neutral salt  $C^4Li^2O^8$ , obtained by saturating a hot solution of oxalic acid with carbonate of lithia, separates on cooling in indistinct, nodular, anhydrous crystals. The salt likewise separates in the anhydrous state from its aqueous solution, on the addition of alcohol. 1 pt. of it dissolves in 13.1 pts. of water at  $19.5^\circ$ .

<i>Crystallised.</i>				<i>Souchay &amp; Lennsen.</i>	
2 LiO .....	29.28	....	28.92	.....	29.07
$C^4O^8$ .....	72.00	....	71.08		
<hr/>					
$C^4Li^2O^8$ .....	101.28	....	100.00		

According to Rammelsberg, the crystals contain 1 At. water.

The *acid salt*,  $C^4HLiO^8 + 2Aq$ , forms large tabular crystals, which dissolve in 12.8 pts. of water at  $17^\circ$ , gave off 2 At. water at  $100^\circ$ , and oxalic acid at  $160^\circ$ .

				Souhay & Lenssen.	
LiO .....	14.64	....	12.88	.....	12.97
$C^4H^6$ .....	72.00	....	63.36		
3 HO .....	27.00	....	23.76		
<hr/>					
$C^4HLiO^8 + 2Aq$ .....	113.64	....	100.00		

It does not appear possible to obtain either a hyperacic oxalate of lithia or a double oxalate of lithia and magnesia.

*Oxalate of Baryta.* The *neutral salt*  $C^4Ba^2O^8 + 2Aq$ , dissolves in 2590 pts. of cold, and 2500 pts. of hot water, more readily in solution of sal-ammoniac, still more in water containing acetic acid, and most readily in aqueous oxalic acid. At  $100^\circ$  it gives off 1 At. water, and is reduced to  $C^4Ba^2O^8 + Aq$ , which is also the composition of the salt obtained by precipitating a solution of chloride of barium with oxalate of ammonia at the boiling heat.

*Acid oxalate of baryta*,  $C^4HBa^2O^8 + 2Aq$ , gives off 1 At. water at  $100^\circ$ , the second At. of water of crystallization at  $125^\circ$ , and at  $140^\circ$ , oxalic acid begins to volatilize (See ix, 129). The crystals require 392 pts. of water at  $17^\circ$  to dissolve them, and are decomposed by hot water, with formation of the neutral salt; alcohol likewise throws down the neutral salt from the aqueous solution of the acid salt.

*Oxalate of Strontia.* The *neutral salt*  $C^4Sr^2O^8$ , is precipitated from soluble strontia-salts by oxalate of ammonia (if precipitated by oxalate of potash, it contains potash), as a loose white powder containing 5 At. water, 1 At. of which (4.07 p. c.) it gives off at  $60^\circ$ , two more at  $100^\circ$ , and the remaining 2 At. at  $150^\circ$ . It is likewise obtained by precipitating a concentrated solution of nitrate or chloride of strontium with a small quantity of oxalic acid. It dissolves in 12000 pts. of cold water, is nearly insoluble in hot concentrated oxalic acid, moderately soluble in ammoniacal salt. Since sulphate of strontia, according to Fresenius, requires only 7000 parts of water to dissolve it, oxalic acid should be a more delicate test for strontia than sulphuric acid; it is however, seldom applicable for that purpose in analysis, on account of the solubility of oxalate of strontia in ammoniacal salts; moreover the delicacy of the reaction with sulphuric acid may be greatly increased by addition of alcohol.

				Souhay & Lenssen.	
				<i>mean.</i>	
2 SrO .....	104	....	47.06	.....	46.61
$C^4H^6$ .....	72	....	32.50	.....	32.23
5 HO .....	45	....	20.56		
<hr/>					
$C^4Sr^2O^8 + 5Aq$ .....	221	....	100.00		

The neutral salt with 2 At. water,  $C^4Sr^2O^8 + 2Aq$  (ix, 129), is obtained by precipitating a boiling solution of nitrate of strontia with oxalate of ammonia, and boiling the precipitate with the liquid for a considerable time. It does not give off any water at  $100^\circ$ . Wicke's salt with 6 At.

water, Souchay & Lenssen were unable to obtain; possibly Wicke analysed a mixture of the neutral and the acid salts, such a mixture being in fact, obtained by precipitating a concentrated solution of oxalic acid with a small quantity of nitrate or chloride of strontium.

*Acid Oxalate of Strontia*,  $C^4HSrO^8 + 2Aq$ , was once obtained by mixing a rather strong solution of chloride of strontium with 1 or 2 measures of strong hydrochloric acid, and 3 or 4 measures of solution of oxalic saturated at  $60^\circ$ . After standing for some days at  $0^\circ$ , the liquid deposited, together with oxalic acid and the neutral salt, crusts of an acid salt, consisting of highly lustrous prismatic crystals, with pyramidal summits, mostly united in geodes. These crystals effloresced in the air, and were resolved by water into free oxalic acid and the neutral salt. They gave by analysis 34.0 p. c. strontia, the formula requiring 34.4 p. c.

*Oxalate of Lime*. — For the salt precipitated from calcium-solutions by alkaline oxalates and dried at a gentle heat, Thomson, Graham, and others gave the formula  $C^4Ca^2O^8 + 4Aq$  (ix, 130). According to E. Schmid (*Ann. Pharm.* 97, 225), the precipitate of oxalate of lime obtained by mixing neutral solutions of chloride of calcium and oxalate of potash, and left to dry for a considerable time at ordinary temperatures in the air, or for a shorter time in vacuo over sulphuric acid, consists of  $C^4Ca^2O^8 + 2Aq$  (water by analysis, 12.3 p. c., by calculation, 12.1). The precipitate thus obtained, did not exhibit distinct angular terminations, even with a magnifying power of  $300^\circ$ ; but that which was produced by slowly adding a solution of oxalate of potash to solution of chloride of calcium, exhibited under the microscope dendrites and laminæ made up of oblique prismatic tables, and appeared to consist of a mixture of the hydrates  $C^4Ca^2O^8 + 4Aq$ , and  $C^4Ca^2O^8 + 2Aq$ .

According to Souchay and Lenssen (*Ann. Pharm.* 100, 308), oxalate of lime, dried in the air at ordinary temperatures, contains sometimes 2 At., sometimes 6 At. water; and when dried at  $100^\circ$ , always 2 At., half of which is given off at  $180^\circ$ , and the remainder at a temperature considerably above  $200^\circ$ ; on exposing the anhydrous salt to the air, the 2 At. water are quickly reabsorbed. A salt with 4 At. water does not appear to exist. — Oxalate lime precipitated at the boiling heat from a mixture of solutions of chloride of calcium and oxalate of ammonia, contains  $C^4Ca^2O^8 + 2Aq$ ; so likewise when precipitated in the cold from concentrated solutions, whether neutral or alkaline; but the salt precipitated in the cold from dilute solutions, is always a mixture of  $C^4Ca^2O^8 + 2Aq$ , and  $C^4Ca^2O^8 + 6Aq$ . — On adding a small quantity of chloride of calcium to a saturated solution of oxalic acid, a precipitate is formed consisting of microscopic crystalline laminæ, and containing  $C^4Ca^2O^8 + 2Aq$ ; and on adding a small quantity of oxalic acid to a large excess of chloride of calcium, a gummy precipitate is obtained of the same composition, and appearing under the microscope as an indistinct crystalline mass; but by adding a small quantity of chloride of calcium to a very dilute solution of oxalic acid, there is formed after awhile, a precipitate consisting of square prismatic crystals of  $C^4Ca^2O^8 + 6Aq$ , together with oblique prismatic (monoclinometric) crystals  $Ca^4Ca^2O^8 + 2Aq$ , the former being in larger proportion as the oxalic acid solution is more dilute.

The square prismatic crystals of oxalate of lime occurring in plants



(*Mamillaria quadrispina*, *Cereus senilis*, *Melocactus macroacanthus*, &c.), are, according to Schmid,  $C^4Ca^2O^8 + 6Aq$ ; they give off two-thirds of their water, slowly when exposed to the air, more quickly in rarefied air. The statement of Lehmann, that these crystals are obtained by mixing dilute solutions of lime-salts and alkaline oxalates, is not confirmed by Schmid's observations.

*Behaviour of Oxalate of Lime with Hydrochloric Acid.* — A solution of oxalate of lime in hot hydrochloric acid, deposits crystals of the salt  $C^4Ca^2O^8 + 2Aq$ . (E. Schmid). According to Souchay & Lenssen, this salt is deposited on cooling, when oxalate of lime is added at  $100^\circ$ , to hydrochloric acid, of sp. gr. less than 1.10, in quantity sufficient to saturate it; but if the solution is not saturated, it deposits after some time, square prismatic crystals, consisting of  $C^4Ca^2O^8 + 6Aq$ . — By adding oxalate of lime to warm hydrochloric acid, of sp. gr. 1.10 or higher, double salts are obtained in scaly crystals, consisting of oxalate and chloride of calcium. With acid of sp. gr. 1.20 Souchay & Lenssen obtained the salt  $2C^4Ca^2O^8 + CaCl + 24HO$ :

					Souchay & Lenssen.
2 $C^4Ca^2O^8$	.....	256.0	....	48.53	..... 47.93 to 50.98
CaCl	.....	55.5	....	10.52	..... 9.51 to 10.91
24 HO	.....	216.0	....	40.95	
<hr/>					
527.5					.... 100.00

Fritzsche's salt  $C^4Ca^2O^8, 2CaCl + 14Aq$  (ix, 132), was not obtained either by Souchay & Lenssen or by Schmid.

With *nitric acid*, oxalate of lime behaves in the same manner as with hydrochloric acid, excepting that it is insoluble in strong nitric acid, and therefore does not yield any oxalo-nitrate. (Souchay & Lenssen). According to Schmid, a solution of oxalate of lime in hot nitric acid, deposits monoclinometric laminæ of the bihydrated salt, the last mother-liquors however, yielding free oxalic acid.

Oxalate of lime is insoluble in hot concentrated solutions of the chlorides of potassium, sodium, ammonium, barium, strontium, and calcium, but soluble to a considerable extent in hot solutions of salts of the metals belonging to the magnesian group, and is precipitated from these solutions by excess of an alkaline oxalate. (Souchay & Lenssen).

Oxalate of lime dissolves in considerable quantity in pure *phosphoric acid*, especially with the aid of heat. Such a solution, when largely diluted with water, remains clear if it contains a large quantity of phosphoric acid; and if caustic soda be then cautiously added, till the precipitate formed at first is redissolved, and the liquid then left to stand quietly, a large proportion of the oxalate of lime crystallizes within 24 hours in quadratic pyramids; and the mother-liquor, if again treated with soda, yields another crop of crystals. (Neubauer, *Ann. Pharm.* 99, 223.)

*Oxalate of Magnesia* is best prepared by neutralizing oxalic acid with carbonate of magnesia, and washing with cold water; when precipitated from a magnesia-salt by oxalate of potash, it always retains potash. — Prepared by the first method, it is a white sandy powder, consisting of  $C^4Mg^2O^8 + 4Aq$ , soluble in 1500 pts. of water at  $16^\circ$ , and in 1300 pts. of

boiling water. It gives off 1·5 p. c. water, at 100°, and does not lose the whole of it even at 140°; but at 150° it becomes anhydrous, at the same time however, suffering partial decomposition.

No acid oxalate of magnesia or double oxalate of magnesia and soda appears to exist.

*Ammonio-magnesian Oxalates.* — A concentrated solution of chloride of magnesium forms, with oxalate of ammonium, a precipitate of oxalate of magnesia, which always contains small quantities of the double oxalate of magnesia and ammonia. But a dilute solution of chloride of magnesium mixed with oxalate of ammonia, especially if a little caustic ammonia is added, yields, after standing for some time, crystalline crusts consisting of oxalate of magnesia and ammonia and oxalate of magnesia in equivalent proportions, varying according as the magnesia or the oxalate of ammonia predominated in the liquid; they dissolve in water with separation of oxalate of magnesia.

*a.*  $2C^4Mg(NH^4)O^8, 5C^4(NH^4)^2O^8 + 18Aq.$  — Obtained by adding oxalate of ammonia to a magnesia solution, rendered strongly alkaline by ammonia and then mixed with a quantity of sal-ammoniac sufficient to redissolve the precipitate,—in such proportion, that the magnesia may be to the oxalic acid ( $C^4H^2O^8 + 4Aq$ ), as 1 : 12·6.

Souhay & Lenssen.					
2 MgO	.....	40	...	3·98	..... 3·98
12 NH <sup>4</sup> O	.....	312	...	49·51	..... 30·41
7 C <sup>4</sup> H <sup>6</sup>	.....	504	...	30·65	..... 49·53
18 HO	.....	162	...	15·91	
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		1018	...	100·00	

*b.*  $5C^4Mg(NH^4)O^8 + 4C^4(NH^4)^2O^8 + 24Aq.$  — By mixing a magnesia solution with oxalate of ammonia, in such proportion that the magnesia may be the oxalic acid, as 1·0 : 6·3.

Souhay & Lenssen.					
5 MgO	.....	100	...	7·68	..... 7·70
13 NH <sup>4</sup> O	.....	388	...	25·98	..... 25·99
9 C <sup>4</sup> O <sup>8</sup>	.....	648	...	49·77	..... 49·61
24 HO	.....	216	...	16·57	
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		1302	...	100·00	

The salt  $C^4Mg(NH^4)O^8 + C^4Mg^2O^8 + 2Aq$  described by Brandes (ix, 183), was not obtained by Souhay & Lenssen.

*c.*  $C^4Mg(NH^4)O^8 + 2C^4(NH^4)^2O^8 + 8Aq.$  — Prepared by gradually adding recently precipitated oxalate of magnesia to a boiling concentrated solution of oxalate of ammonia, till the former no longer dissolves, even after long boiling. On filtering hot, and leaving the liquid to cool quietly, the salt *c* separates in hard, warty, crystalline crusts, having the appearance of enamel, slightly translucent, and efflorescing in the air. It dissolves pretty readily in water, with partial separation of oxalate of magnesia; in ammoniacal salts it forms a clear solution.— At 100° it gives off 13·3 p.c. (rather more than 6 At.) water; at 120°,

7 At. in all; at 140° it begins to decompose and assume a brownish tint.

					Souchay & Lenssen.
MgO	.....	20	....	4.56	..... 4.51
5 NH <sup>4</sup> O	.....	130	....	29.69	..... 29.83
3 C <sup>4</sup> O <sup>6</sup>	.....	216	....	49.31	..... 49.26
8 HO	.....	72	....	16.44	
<hr/> C <sup>4</sup> Mg(NH <sup>4</sup> )O <sup>8</sup> + 2C <sup>4</sup> (NH <sup>4</sup> ) <sup>2</sup> O <sup>8</sup> + 8Aq ....					438 .... 100.00

d. C<sup>4</sup>Mg(NH<sup>4</sup>)O<sup>8</sup> + 3C<sup>4</sup>(NH<sup>4</sup>)<sup>2</sup>O<sup>8</sup> + 8Aq. — When the mother-liquor from which the preceding salt has crystallized is mixed with a little water and ammonia, and set aside for some weeks in the cold, it deposits milk-white crusts, which dissolve in water with partial decomposition, the solution becoming turbid. It gives off 12.15 p. c. (about 8 At.) water at 100°.

					Souchay & Lenssen.
MgO	.....	182	....	3.56	..... 3.56
7 NH <sup>4</sup> O	.....	20	....	32.39	
4 C <sup>4</sup> O <sup>6</sup>	.....	288	....	51.24	..... 51.26
8 HO	.....	72	....	12.81	
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562 ....					100.00

*Oxalate of Glucina and Ammonia.* C<sup>4</sup>G(NH<sup>4</sup>)O<sup>8</sup>. — According to Senarmont and Rammelsberg (*Jahresb. d. Chem.* 1857, 295) the crystals of this salt belong to the right prismatic (rhombic) system, exhibiting the faces  $\infty \check{P} \infty . \infty \bar{P} \infty . oP . P . 2P . \infty P . \check{P} \infty . \bar{P} \infty . 2\bar{P} \infty . 4\bar{P} \infty .$  Ratio of the axes = 0.8759 : 1 : 1.7413. Inclination of the faces, P : P in the brachydiagonal principal section = 121° 50'; in the macrodiagonal = 111° 24'; in the basic section = 98° 44'; 2P : 2P in all three sections = 105° 56'; 93° 10' and 132° 4'. —  $\infty P : \infty \bar{P} \infty = 138^\circ 47'$ ;  $oP : \check{P} \infty = 143^\circ 27'$ ;  $oP : \bar{P} \infty = 139^\circ 45'$ .

*Oxalate of Manganese.* — This salt, whether prepared by precipitating the sulphate or chloride of manganese with oxalic acid, or by treating the carbonate of manganese or manganoso-manganic oxide with oxalic acid, contains, in the air-dried state, 5 At. water. Souchay & Lenssen (*Ann. Pharm.* 102, 47) found in it, 37.55 p. c. MnO, the formula C<sup>4</sup>Mn<sup>2</sup>O<sup>8</sup> + 5Aq requiring 37.83 p. c. 1 pt. of this hydrated salt dissolves in 2460 pts. of cold, and in 1250 pts. of boiling water; but the solubility is very greatly increased by the presence of a trace of oxalate of potash or oxalate of ammonia. At 100°, according to Souchay & Lenssen, it gives off all its water (as previously found by Liebig, *Ann. Pharm.* 95, 116). After drying at that temperature, it yielded 48.52 and 49.09 p. c. MnO, the formula C<sup>4</sup>Mn<sup>2</sup>O<sup>8</sup> requiring 49.72 p. c.

The results just detailed are at variance with those obtained by other chemists. According to Graham (ix, 146), the salt contains 5 At. water, the whole of which it retains at 100°; according to Hausmann & Löwenthal, it contains after drying at 100° 4 At. water.

According to H. Croft (*Chem. Gaz.* 1857, 62), the quantity of water contained in manganous oxalate varies with the temperature at which it is precipitated. Hot concentrated solutions of manganous sulphate and

oxalic acid yield a white granular precipitate consisting of  $C^4M^2O^8 + 4Aq$ , which does not give off any water at  $100^\circ$ . (This agrees with the statement of Hausmann & Löwenthal.) In a solution of manganous sulphate in 30 pts. of water, oxalic acid produces a precipitate which has a faint violet colour, but in a few days becomes white and granular, and exhibits the same composition. When manganous sulphate, dissolved in 30 to 100 parts of water is precipitated by oxalate of potash, a pale violet crystalline precipitate is obtained, resembling benzoic acid and containing  $C^4M^2O^8 + 6Aq$ . It is unalterable in the air at ordinary temperatures, but at  $100^\circ$  gives off 2 At. water and turns white. When heated for some time in the air, it yields red crystalline manganic oxide. (Croft). — These statements are confirmed by Georgen (*Compt. rend.* 47, 929). Oxalic acid mixed with excess of manganous sulphate in the cold, yields rose-coloured prismatic needles of the salt  $C^4Mn^2O^8 + 6Aq$ ; but when a very hot solution of oxalic acid is mixed with a hot solution of a manganous salt till a precipitate begins to form, and the liquid is then left to cool, white flattened octohedrons are obtained, consisting of  $C^4M^2O^8 + 4Aq$ . — The red salt, when dried in the air, gives off 2 At. water and turns white; but in vacuo and even at  $95^\circ$ , it retains its red colour, although it loses the greater part of its water.

*Ammonio-manganous Oxalate.* — Oxalate of manganese forms with oxalate of ammonia, a series of double salts analogous to the oxalate of ammonia and magnesia, to which Souchay & Lenssen assign the general formula  $x C^4Mn(NH^4)O^8 + 2 C^4Mn(NH^4)^2O^8 + 8Aq$ , the composition varying according to the degree of dilution and the proportions in which the constituent salts are mixed.

*a.*  $C^4Mn(NH^4)O^8 + 2Aq$  is obtained by adding oxalate of manganese to a boiling saturated solution of oxalate of ammonia, and filtering the rose-coloured solution while still hot. The crystalline crusts composed of microscopic square prisms, which first separate from the liquid, consist of the salt *a*. The mother-liquor yields crystals of different composition.

					Souchay & Lenssen.
MnO	.....	35.6	...	23.48	..... 24.18
NH <sup>4</sup> O	.....	26.0	...	17.16	
C <sup>4</sup> O <sup>8</sup>	.....	72.0	...	47.49	..... 46.83
2 HO	.....	18.0	...	11.87	
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151.6					... 100.00

*b.*  $2 C^4Mn(NH^4)O^8 + C^4(NH^4)^2O^8 + 8Aq$ . — The mother-liquor of the salt *a*, filtered and left to itself for 24 hours, deposited crystalline crusts consists of microscopic prisms, which gave by analysis 15.24 p. c. MnO and 46.20 C<sup>4</sup>O<sup>8</sup>, the formula of salt *b* requiring 15.37 MnO and 46.63 C<sup>4</sup>O<sup>8</sup>.

*c.*  $C^4Mn(NH^4)O^8 + 2 C^4(NH^4)^2O^8 + 8Aq$ . — The mother-liquor of *b* mixed with water, yielded, after standing for a day, crystalline crusts containing 7.44 p. c. MnO, and 47.48 p. c. C<sup>4</sup>O<sup>8</sup>; the formula *c* requires 7.84 p. c. MnO and 47.57 C<sup>4</sup>O<sup>8</sup>.

*d.* The mother-liquor of *c* deposits, after standing for some time, crystalline crusts containing 6.19 p. c. MnO and 49.82 C<sup>4</sup>O<sup>8</sup>, agreeing with the formula  $C^4Mn(NH^4)O^8 + 3 C^4(NH^4)^2O^8 + 8Aq$ , which requires 6.17 MnO and 49.86 C<sup>4</sup>O<sup>8</sup>.

All these salts are decomposed by water and effloresce rapidly in the air. The colour is reddish or white, according to the proportions of manganese contained in them. Those which contain a large proportion of manganese separate in small prisms, while those with a smaller quantity of manganese are deposited in crystalline crusts or nodules, and always after the solution has been left at rest for some time.

*e. Oxalate of Manganese and Manganammonium.*  $C^4Mn(N,H^3Mn)O^8 + 6Aq.$  — When a boiling solution of oxalate of ammonia is saturated with oxalate of manganese, the liquid filtered, and ammonia added till the filtrate smells slightly of it, a white or slightly green crystalline powder is precipitated, consisting of transparent microscopic crystals, which have the form of square prisms, but are so much truncated that they are scarcely distinguishable from cubes.

				Souhay & Lenssen.	
2 MnO	.....	71.2	....	33.24	..... 32.62
NH <sup>3</sup>	.....	17.0	....	7.93	..... 7.79
C <sup>4</sup> O <sup>8</sup>	.....	72.0	....	33.61	..... 31.52
6 HO	.....	54.0	....	25.22	
				214.2	.... 100.00

Winkelblech assigned to a salt prepared in a similar manner, the formula  $2NH^3, C^4Mn(NH^4)O + C^4Mn^2O^8 + 8Aq$ , the accuracy of which is called in question by Gmelin (ix, 147).

The salt decomposes quickly in contact with water, turning brown and absorbing oxygen. At 100°, it gives off 6 At. water, assuming at the same time a faint brown colour. (Souhay & Lenssen.)

*Potassio-manganous Oxalate.*  $C^4MnKO^8 + 2Aq.$  — Obtained in reddish crusts by adding manganous oxalate to a boiling concentrated solution of oxalate of potash, and leaving the filtrate to cool. Gives off all its water at 100°. (Souhay & Lenssen, *Ann. Pharm.* 102, 48.)

				Souhay & Lenssen.	
KO	.....	47.2	....	27.27	..... 26.42
MnO	.....	35.6	....	20.61	..... 20.90
C <sup>4</sup> O <sup>8</sup>	.....	72.0	....	41.69	
2 HO	.....	18.0	....	10.43	
				C <sup>4</sup> MnKO <sup>8</sup> + 2Aq....	172.8 .... 100.00

*Potassio-manganic Oxalate* is best obtained by saturating 8 pts. of oxalic acid with carbonate of potash, adding 4 pts. of oxalic acid, and then peroxide of manganese till the liquid exhibits but a faint acid reaction. The purple liquid thus formed is very easily decomposed by light and heat. Mixed with alcohol in the dark and in a vessel externally cooled, it deposits potassio-manganic oxalate (probably  $Mn^2O^3, 3KO, 3C^4O^8 + 6Aq$ ) in purple-red crystals which however cannot be dried without decomposition (Souhay & Lenssen, *Ann. Pharm.* 105, 256.)

*Sodio-manganous Oxalate.* Oxalate of manganese dissolves pretty freely in warm oxalate of soda, and the solution deposits crystalline crusts containing variable quantities of manganese, and probably consisting of oxalate of soda having oxalate of manganese mechanically inclosed within it. (Souhay & Lenssen, *Ann. Pharm.* 102, 49-.)

*Oxalate of Arsenious Acid and Potash.* — Finely pulverized arsenious acid dissolves in a concentrated boiling solution of oxalic acid, but separates again on cooling, not appearing to combine with it; but a hot solution of binoxalate of potash dissolves arsenious acid much more readily, and the solution on cooling deposits small hard crystals having a fine glassy lustre. They gave by analysis 20.47 p. c.  $\text{AsO}_3$  and 25.94 p. c.  $\text{KO}$ , and probably consist of  $\text{AsO}_3, 3\text{KO}, 3\text{C}^4\text{O}^6 + 6\text{Aq}$ , which requires 19.4  $\text{AsO}_3$  and 27.7  $\text{KO}$ . (Souhay & Lenssen, *Ann. Pharm.* 105, 255.)

*Oxalate of Antimony.*  $\text{C}^4(\text{H}, \text{SbO}^3)\text{O}^8 + \text{Aq}$ . — Souhay & Lenssen prepared this salt by mixing a saturated aqueous solution of oxalic acid with a solution of terchloride of antimony in hydrochloric acid: it separates in the course of 24 hours, as a granular precipitate containing 61.14 p. c. teroxide of antimony and 31.33 p. c.  $\text{C}^4\text{O}^6$ . The formula  $\text{C}^4(\text{H}, \text{SbO}^3)\text{O}^8 + \text{Aq}$  or  $\text{SbO}^3, \text{C}^4\text{O}^6 + 2\text{Aq}$  requires 61.58  $\text{SbO}^3$  and 30.73  $\text{C}^4\text{O}^6$ .

The salt gives off 1 At. at  $100^\circ$  and begins to decompose at  $220^\circ$ . (Souhay & Lenssen.) It was originally obtained by Peligot (ix, 148), who assigned to it the formula  $\text{C}^4(\text{H}, \text{SbO}^3)\text{O}^8$ , requiring 65.88 p. c.  $\text{SbO}^3$ . Peligot's analysis gave 66.15 p. c.

*Ammonio-antimonio Oxalate.*  $\text{SbO}^3, 3\text{NH}^4\text{O}, 3\text{C}^4\text{O}^6 + 4\text{Aq}$ . — Obtained by mixing a solution of teroxide of antimony in acid oxalate of ammonia, first with a small quantity of absolute alcohol (which throws down acid oxalate of ammonia), then, after filtering, with about three times its volume of absolute alcohol.

						Souhay & Lenssen.	
$\text{SbO}^3$	.....	144	....	30.39	.....	30.23	.... 29.89
3 $\text{NH}^4\text{O}$	.....	78	....	16.45	.....	15.87	
3 $\text{C}^4\text{O}^6$	.....	216	....	45.57	.....	45.87	
4 $\text{HO}$	.....	36	....	7.59			
						<hr/>	
						474	.... 100.00

May be regarded either as  $\text{C}^{12}\text{Sb}''(\text{NH}^4)^3\text{O}^{24} + 4\text{HO}$  or as  $\text{C}^{12}(\text{H}^3, \text{Sb}^4\text{O}^2, \text{NH}^4)^3\text{O}^{24} + 2\text{HO}$ .

*Potassio-antimonio Oxalate.*  $\text{SbO}^3, 3\text{KO}, 3\text{C}^4\text{O}^6 + 12\text{Aq}$ . — Obtained by dissolving teroxide of antimony in a hot concentrated solution of acid oxalate of potash. The filtrate, as it cools, deposits nodular crystals of the salt, which dissolve without decomposition in water, but are decomposed by mineral acids, with separation of oxalic acid or of basic oxalate of antimony. Gives off 6 At. water at  $100^\circ$ . (Souhay & Lenssen.)

						Souhay & Lenssen.	
$\text{SbO}^3$	.....	144.0	....	23.67	.....	23.20	.... 23.84
3 $\text{KO}$	.....	141.3	....	23.19	.....		.... 23.67
3 $\text{C}^4\text{O}^6$	.....	216.0	....	35.43			
12 $\text{HO}$	.....	108.0	....	17.71			
						<hr/>	
						609.3	.... 100.00

=  $\text{C}^{12}\text{Sb}''\text{K}^3\text{O}^{24} + 12\text{HO}$  or  $\text{C}^{12}(\text{H}^3, \text{K}^3, \text{SbO}^3)\text{O}^{24} + 10\text{HO}$ .

*Sodio-antimonio Oxalate.*  $\text{SbO}^3, 3\text{NaO}, 3\text{C}^4\text{O}^6 + 2\text{NaO}, \text{C}^4\text{O}^6 + 20\text{Aq}$  or  $\text{C}^{12}(\text{H}^3, \text{Na}^3, \text{SbO}^3)\text{O}^{24} + \text{C}^3\text{Na}^3\text{O}^8 + 28\text{Aq}$ . — Prepared like the potash-

salt. Forms distinct highly lustrous crystals, which give by analysis 18.63 p. c.  $\text{SbO}^3$  and 19.88  $\text{NaO}$ , the formula requiring 18.81  $\text{SbO}^3$  and 20.20  $\text{NaO}$ . When heated for some time at  $100^\circ$ , it gives off 10 At. water. Dissolves without decomposition in water, either hot or cold, but is decomposed by mineral acids. Sparingly soluble in alcohol, insoluble in ether. (Souhay & Lenssen, *Ann. Pharm.* 105, 252.)

*Oxalate of Bismuth.*  $2\text{BiO}^3, 3\text{C}^4\text{O}^6 + 15\text{Aq} = \text{C}^{12}\text{Bi}^{\text{III}}\text{O}^{24} + 15\text{Aq}$ . — Separates as a white crystalline precipitate on mixing nitrate of bismuth with excess of oxalic acid. Retains 2 At. water at  $100^\circ$ , but decomposes at higher temperatures into suboxide of bismuth ( $\text{BiO}^3$ ) and [acid] oxalate of bismuth. It is insoluble in water, soluble in acids, and decomposes, by prolonged contact with water, into oxalic acid which dissolves and a basic oxalate of bismuth. (Souhay & Lenssen.)

Souhay & Lenssen.					
2 $\text{BiO}^3$ .....	464	...	56.93	.....	56.67 ... 56.95 ... 56.77
3 $\text{C}^4\text{O}^6$ .....	216	...	26.50	.....	26.82
15 HO .....	135	...	16.57		
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	815	...	100.00		

For the *basic oxalate of bismuth* (ix, 150) Heintz found the formula  $2(\text{BiO}^3, \text{C}^4\text{O}^6) + 3\text{Aq}$ . — Souhay & Lenssen, by boiling the recently precipitated normal oxalate with water, till the liquid no longer became acid, obtained a salt which gave by analysis 72.39 p. c. oxide, agreeing with the formula  $\text{BiO}^3, \text{C}^4\text{O}^6 + 2\text{Aq}$  or  $\text{BiO}^3, \text{C}^{12}(\text{Bi}^{\text{III}})^2\text{O}^{24} + 6\text{Aq}$  (requiring 72.05 p. c.  $\text{BiO}^3$ ), better than with Heintz's formula which requires 73.5 p. c.

*Oxalate of Bismuth and Ammonium.*  $\text{C}^{12}\text{Bi}^{\text{III}}(\text{NH}^4)^3\text{O}^{24} + 6\text{C}^4(\text{NH}^4)^3\text{O}^8 + 24\text{Aq}$ . — Crystallizes from a hot saturated solution of oxalate of bismuth in oxalate of ammonia, in small prismatic crystals which give off the whole of their water (13.98 p. c.) at  $100^\circ$ . Dissolves readily in hot water, forming a clear solution which becomes turbid after a few seconds, and deposits oxalate of bismuth as a crystalline powder. It is insoluble in alcohol and ether.

Souhay & Lenssen.					
$\text{BiO}^3$ .....	232	...	15.61	.....	15.92
15 $\text{NH}^4\text{O}$ .....	390	...	26.24	.....	25.92
9 $\text{C}^4\text{O}^6$ .....	648	...	43.61	.....	42.66
24 HO .....	216	...	14.54	.....	13.98
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	1486	...	100.00	.....	98.48

*Oxalate of Bismuth and Potassium.*  $\text{BiO}^3, 3\text{KO}, 3\text{C}^4\text{O}^6 + 2(2\text{KO}, \text{C}^4\text{O}^6) + 24\text{Aq}$  or  $\text{C}^{12}\text{Bi}^{\text{III}}\text{K}^3\text{O}^{24} + 2\text{C}^4\text{K}^2\text{O}^8 + 24\text{Aq}$ . — Prepared like the preceding, and separates in small prismatic crystals which are insoluble in alcohol and ether, and are decomposed by water. They give by analysis, 20.45 p. c.  $\text{BiO}^3$  and 27.78 p. c.  $\text{KO}$ , the formula requiring 20.39  $\text{BiO}^3$  and 28.99  $\text{KO}$ . (Souhay & Lenssen.)

The mother-liquor deposits a salt containing 15.53 p. c.  $\text{BiO}^3$ , corresponding nearly to the formula  $\text{C}^{12}\text{Bi}^{\text{III}}\text{K}^3\text{O}^{24} + 4\text{C}^4\text{K}^2\text{O}^8 + 24\text{Aq}$ . (Souhay & Lenssen.)

It does not appear possible to prepare an oxalate of bismuth and sodium.



*Oxalate of Cadmium.*  $C^4Ca^2O^8 + 6Aq.$  — The anhydrous salt is obtained as a white amorphous powder, by digesting carbonate of cadmium with oxalic acid. Oxalic acid or oxalate of ammonia added to chloride of cadmium throws down the six-hydrated salt, as a white precipitate consisting of microscopic tubular crystals. Soluble in 13000 pts. of cold and 11000 pts. of boiling water; a little more soluble in water and oxalic acids; easily soluble in mineral acids, ammonia and ammoniacal salts. Gives off all its water at  $100^\circ$ , and is decomposed at  $340^\circ$ , leaving a mixture of oxide of cadmium ( $CdO$ ) and metallic cadmium. Marchand's statement that the residue thus obtained consists of  $Cd^2O$ , is not confirmed by the observations of Souchay & Lenssen.

At $100^\circ$ .				Souchay & Lenssen.	
2 $CdO$	.....	127.5	....	63.90	..... 63.45
$C^4O^8$	.....	72.0	....	36.10	
<hr/>					
$C^4Cd^2O^8$	.....	199.5	....	100.00	

Hydrated.				Souchay & Lenssen.	
2 $CdO$	.....	127.5	....	50.30	..... 49.89
$C^4O^8$	.....	72.0	....	28.40	
6 $HO$	.....	54.0	....	21.30	
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$C^4Cd^2O^8 + 6Aq$	....	253.5	....	100.00	

*Oxalate of Cadmammonium.*  $C^4(NH^3Cd)^2O^8 + 4Aq.$  — When oxalate of cadmium is added to ammonia till no more is dissolved on heating the liquid, the filtrate, left for some time in the cold, deposits needle-shaped crystals, which rapidly give off part of their ammonia when exposed to the air, and at  $100^\circ$  give off water as well as ammonia, acquiring at the same time a slight brownish tint, from separation of oxide of cadmium.

				Souchay & Lenssen.	
2 $CdO$	.....	127.5	....	47.31	..... 47.81 .... 47.25
2 $NH^3$	.....	84.0	....	12.62	..... 10.21
$C^4O^8$	.....	72.0	....	26.72	..... .... 26.19
4 $HO$	.....	36.0	....	13.35	
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				269.5	.... 100.00

The deficiency of ammonia arose from the spontaneous decomposition of the crystals.

*Oxalate of Cadmium and Ammonium.* — a.  $2C^4Cd(NH^4)O^8 + 5C^4(NH^4)^2O^8 + 18Aq.$  — Separates in microscopic crystals when a solution of oxalate of cadmium in oxalate of ammonia, saturated at the boiling heat, is diluted, after filtration, with an equal volume of water. Gives off all its water at  $100^\circ$ .

				Souchay & Lenssen.	
2 $CaO$	.....	127.5	....	11.57	..... 11.21 .... 11.42
12 $NH^4O$	.....	312.0	....	28.21	..... 28.00
7 $C^4O^8$	.....	504.0	....	45.57	..... 45.44
18 $HO$	.....	162.0	....	14.65	
<hr/>					
				1105.5	.... 100.00



b.  $2\text{C}^{\text{d}}\text{Cd}(\text{NH}^{\text{d}})\text{O}^{\text{s}} + 7\text{C}^{\text{d}}(\text{NH}^{\text{d}})^2\text{O}^{\text{s}} + 22\text{Aq.}$  — Separates in hard crystalline crusts from the preceding saturated solution if left to cool without addition of water.

Souhay & Lenssen.					
2 CdO	.....	127.5	...	9.17	..... 8.62
16 NH <sup>d</sup> O	.....	416.0	...	29.94	..... 29.72
9 C <sup>d</sup> O <sup>s</sup>	.....	648.0	...	46.64	..... 46.35
22 HO	.....	198.0	...	14.25	
<hr/>					
		1389.5	...	100.00	

c. The salt obtained by dissolving oxide of cadmium in oxalate of ammonia, to which Rammelsberg (x, 532) assigned the formula  $2\text{C}^{\text{d}}\text{Cd}(\text{NH}^{\text{d}})\text{O}^{\text{s}} + 3\text{C}^{\text{d}}(\text{NH}^{\text{d}})^2\text{O}^{\text{s}} + 18\text{Aq}$  is supposed by Souhay & Lenssen to contain only 14Aq. The three double-salts then form a regular series, their formulæ being, if A stand for  $\text{C}^{\text{d}}\text{Cd}(\text{NH}^{\text{d}})\text{O}^{\text{s}}$ , and B for  $\text{C}^{\text{d}}(\text{NH}^{\text{d}})^2\text{O}^{\text{s}}$ :

2 A	+	7 B	+	22 Aq
2 A	+	5 B	+	18 Aq
2 A	+	3 B	+	14 Aq

*Oxalate of Cadmium and Potassium.*  $\text{C}^{\text{d}}\text{CdKO}^{\text{s}} + 2\text{Aq.}$  — Produced by saturating a boiling solution of oxalate of potash with oxalate of cadmium, and separates from the filtrate in microscopic square-based octohedrons, which give off their water at 100° and are decomposed by water.

Souhay & Lenssen.					
CaO	.....	63.7	...	31.72	..... 31.29
KO	.....	47.1	...	23.45	..... 22.91
C <sup>d</sup> O <sup>s</sup>	.....	72.0	...	35.86	
2 HO	.....	18.0	...	8.97	
<hr/>					
$\text{C}^{\text{d}}\text{KCdO}^{\text{s}} + 2\text{Aq}$	.....	200.8	...	100.00	

*Oxalate of Cadmium and Sodium.*  $\text{C}^{\text{d}}\text{CdNaO}^{\text{s}} + 2\text{Aq.}$  — Similar to the potassium-salt. By analysis: 33.95 p. c. CdO and 17.3 NaO, the formula requiring 34.6 CdO and 16.8 NaO. (Souhay & Lenssen.)

*Stannous Oxalate.* — This salt treated with warm caustic ammonia yields white stannous hydrate, but with a somewhat concentrated solution of caustic potash, it yields anhydrous stannous oxide. Hydrochloric acid at the boiling heat dissolves an almost unlimited quantity of stannous oxalate: and, as the solution cools, the whole of the oxalic acid is deposited in crystals, while protochloride of tin remains in solution; but if a little water be added to the solution, stannous oxalate crystallizes out. (R. Böttger, *J. pr. Chem.* 76, 238.)

*Ferrous Oxalate.* — When lemon-yellow ferrous oxalate,  $\text{C}^{\text{d}}\text{Fe}^2\text{O}^{\text{s}} + 4\text{Aq}$ , is heated with *mono-hydrated sulphuric acid*, carbonic oxide and carbonic acid are given off, and pure ferrous sulphate remains in the form of a soft white powder. But if the same salt be heated with *dilute sul-*

phuric acid, the liquid after cooling yields crystals of oxalic acid, and ferrous sulphate remains in solution. — When ferrous oxalate is dissolved to saturation in strong *hydrochloric acid* at the boiling heat, the liquid when quite cold, deposits, large transparent crystals of oxalic acid, and afterwards crystals of ferrous chloride.

If ferrous oxalate be added to boiling solution of *caustic potash*, the boiling heat being continued for some time, a velvet-black precipitate of ferrous oxide is produced, which however soon passes on the filter to a higher state of oxidation. — Ferrous oxalate boiled with a concentrated solution of bicarbonate of potash, yields a perfectly white precipitate of ferrous carbonate, which likewise oxidizes quickly during washing. (Böttger, *loc. cit.*)

The salt  $C^4Fe^2O^8 + 4Aq$ , dissolves in 4500 pts. of cold and 3800 pts. of hot water. (Souchay & Lenssen.)

*Potassio-ferrous Oxalate.*  $C^4FeKO^8 + 2Aq$ . — A solution of ferrous oxalate in oxalate of potash, deposits, when mixed with alcohol and left to stand for 24 hours, oily drops of potassio-ferrous oxalate, which soon solidify. Analysis gave 27.1 p. c. KO, the formula requiring 27.2 p. c. (Souchay & Lenssen, *Ann. Pharm.* 105, 255.)

*Mercurous Oxalate.*  $C^4(Hg_2)^2O^8$ . — Obtained in the anhydrous state by heating mercuric oxalate to  $164^\circ$ . It is also produced by heating mercurous nitrate with excess of oxalic acid, as a white precipitate, which is insoluble even in hot water, and obstinately retains hygroscopic water, from which indeed, it cannot be freed without decomposing into mercuric oxalate and metallic mercury, this decomposition taking place at  $100^\circ$ . The same products are obtained when mercurous oxide  $Hg^2O$ , is heated with oxalic acid. — The anhydrous salt obtained by the first method, begins to decompose only at  $175^\circ$ .

Souchay & Lenssen.					
2 $Hg^2O$	.....	416	...	85.24	..... 84.67
$C^4O^8$	.....	72	...	14.76	
<hr/>					
$C^4(Hg_2)^2O^8$	.....	488	...	100.00	

Harff (ix, 167) supposes it to contain 1 At. water in the state of combination.

Mercurous oxalate is insoluble in oxalic acid, easily soluble in hot nitric acid; in cyanide and sulphocyanide of potassium, it dissolves very easily, with separation of metallic mercury; it is also somewhat soluble in ammonia-salts. Heated with oxalate of potash, soda, or ammonia, it forms double mercuric oxalates, with separation of mercury. It detonates when heated. — With ammonia, it forms a greyish black powder, supposed by Harff to be  $3Hg^2O, NH^3, C^2O^3$ ; it does not however, appear to be of constant composition. (Souchay & Lenssen.)

*Mercuric Oxalate.*  $C^4Hg^2O^8$ . Obtained pure, as a white amorphous powder, by adding a solution of mercuric nitrate to excess of oxalic acid, or by prolonged digestion of yellow mercuric oxide with oxalic acid.

Souchay & Lenssen.					
2 $HgO$	.....	216	...	75	..... 74.49 .... 74.13
$C^4O^8$	.....	72	...	25	
<hr/>					
$C^4Hg^2O^8$	.....	288	...	100	

It is decomposed by heat, giving off carbonic acid and metallic mercury. When dry, it detonates violently on being rubbed. It is easily soluble in hydrochloric acid, less soluble in cold nitric acid, insoluble in oxalic acid. It is decomposed by carbonate and phosphate of soda. Heated with solution of sal-ammoniac, it gives off carbonic acid, and yields oxalate of ammonia and subchloride of mercury. (Souchay & Lenssen, *Ann. Pharm.* 102, 42).

*Ammonio-mercuric Oxalate.*  $C^4Hg(NH^4)O^8 + 2Aq$ . Precipitated on adding recently precipitated mercuric oxalate to a boiling concentrated solution of neutral oxalate of ammonia, in white microscopic needles, easily decomposed by light [and heat. Loses 12.5 p. c. of its weight at  $100^\circ$ , and decomposes with a hissing noise at a higher temperature, leaving no residue. It is decomposed by water, and does not dissolve in alcohol or ether.

Souchay & Lenssen.					
HgO .....	108	...	48.22	.....	49.60
NH <sup>4</sup> O .....	26	...	11.60	.....	13.24
C <sup>4</sup> O <sup>6</sup> .....	72	...	32.14		
2 HO .....	18	...	8.04		
<hr/>					
$C^4Hg(NH^4)O^8 + 2Aq$ ....	224	...	100.00		

*Potassio-mercuric Oxalate.*  $C^4HgKO^8 + 2Aq$ . — Prepared like the preceding. Small, white, beautifully iridescent, crystalline scales, which under the microscope appear like square prisms. It is decomposed by water, gives off water and turns black at  $100^\circ$ , and is partially decomposed by light.

Souchay & Lenssen.					
HgO .....	108.0	...	44.07	.....	44.60
KO .....	47.1	...	19.22	.....	19.46
C <sup>4</sup> O <sup>6</sup> .....	72.0	...	29.37		
2 HO .....	18.0	...	7.34		
<hr/>					
$C^4HgKO^8 + 2Aq$ .....	245.1	...	100.00		

Mercuric oxalate does not dissolve in oxalate of soda.

*Oxalate of Silver.*  $C^4Ag^2O^8$ . — Obtained [pure and anhydrous as a white crystalline precipitate, by adding oxalic acid to nitrate of silver.

The salt thus prepared, gave by analysis 75.73 p. c. AgO, the formula requiring 76.31 p. c. (Souchay and Lenssen). — It is very sparingly soluble in cold, somewhat more in hot water, perfectly insoluble in alcohol and ether. It dissolves readily in ammonia and carbonate of ammonia; the solution turns brown when exposed to light, and when slowly evaporated in the dark, yields the oxalate of silver in large, hard, shining prisms. It decomposes between  $110^\circ$  and  $150^\circ$ , and detonates when suddenly heated. With *iodide of methylene*, oxalate of silver yields bioxy-methylene,  $C^4H^4O^4$ , together with iodide of silver, and a mixture of carbonic acid and carbonic oxide. (Butlerow, p. 389). — With *chloride of benzylene*,  $C^{14}H^6Cl^2$ , it yields by a similar reaction, bitter almond oil:



With *iodide of ethylene* on the contrary, it yields nothing but iodide of silver and a mixture of carbonic acid and carbonic oxide;



Similarly with *bromide of amylene*. (Golowkinsky, *Ann. Pharm.* 111, 252.)

*Ammonio-oxalate of Silver*,  $\text{C}^4\text{Ag}^2\text{O}^3, 4\text{NH}^3$ , or *Oxalate of Biammonbiargentammonium*,  $\text{C}^4\text{O}^3, \text{N}^2\{\text{H}^6, \text{N}^2(\text{H}^6\text{Ag}^2)\}$ , is obtained as a spongy tumefied mass, by passing dry ammonia-gas over dry oxalate of silver. It is easily soluble, has an alkaline reaction, and is decomposed by acids, with separation of oxalate of silver. (Souhay & Lenssen.)

Souhay & Lenssen.				
2 AgO .....	232	....	62.37	
C <sup>4</sup> O <sup>3</sup> .....	72	....	19.35	
4 NH <sup>3</sup> .....	68	....	18.28	..... 17.30
<hr/>				
	372	....	100.00	

Oxalate of silver does not form double salts with the alkaline oxalates. (Souhay & Lenssen.)

*Sodio-platinous Oxalate*.  $\text{C}^4\text{PtNaO}^3 + 4\text{Aq}$ . — Mistaken by Döbereiner for platinous oxalate (ix, 170). Obtained by treating platinate of soda with oxalic acid. The bioxide of platinum is reduced, with effervescence, to protoxide, and the solution, which has first a red, then a violet, and ultimately a deep indigo-colour, deposits the double salt in dark copper-coloured needles. The first crop of crystals gave by analysis, 44.44 p. c. PtO, and 12.00 NaO, the formula requiring 43.49 PtO, and 12.60 NaO. A second crop gave more soda and less platinum. — The salt when moist, is decomposed by exposure to the air. It dissolves in hot water, forming a greenish solution, which becomes blue by evaporation, and is decolorized by hydrochloric acid. Insoluble in alcohol and in ether. (Souhay & Lenssen, *Ann. Pharm.* 105, 256.)

Page 185.

### Iodacetic Acid. $\text{C}^4\text{H}^3\text{IO}^4$

PERKIN & DUPPA. *Phil. Mag.* [4], 18, 54.

Produced as an ethyl-compound by the action of iodide of potassium on bromacetate of ethyl (xii, 534).



It is not produced by the action of chlorine or of chloride of iodine on acetic acid.

*Preparation.* Bromacetate of ethyl, diluted with three times its volume of alcohol, is mixed with an equivalent quantity of iodide of

potassium in fine powder; the mixture is digested for about two hours, at 40°, in the dark; the alcohol is distilled off, after the liquid has been filtered to separate the bromide of potassium; and the residual iodacetate of ethyl is washed with water to separate any remaining bromide of potassium.

To obtain the free acid, the iodacetic ether is first converted into a baryta-salt by digestion in the cold with hydrate of baryta; the excess of baryta is removed by carbonic acid; the filtrate carefully evaporated and allowed to crystallize; the crystals of iodacetate of baryta are dissolved in water; and the solution is decomposed by cautious addition of sulphuric acid. The resulting acid liquid concentrated in vacuo over oil of vitriol, yields crystals of iodacetic acid, which may be purified by two or three crystallizations.

*Properties.* Crystallizes in thin, tough, colourless, rhombohedral plates, which when pressed together, exhibit the aspect of mother-of-pearl. It is not deliquescent, has a very sour taste, melts at 82° with slight decomposition, and solidifies again at 81·5°.

Perkin & Duppa.					
4 C .....	24	...	12·84	.....	12·83
3 H .....	3	...	1·60	.....	1·58
I .....	127	...	68·42	.....	67·89
3 O .....	32	...	17·14	.....	17·70
<hr/>					
C <sup>4</sup> H <sup>3</sup> IO <sup>4</sup> .....	186	...	100·00	.....	100·00

Iodacetic acid is decomposed by moist oxide of silver, in the same manner as bromacetic acid (xii, 533), the iodine being removed and glycolic acid formed :



*Iodacetate of Ammonia* is a very soluble, crystalline, non-deliquescent salt. — The *potash-salt* exhibits similar properties.

*Iodacetate of Baryta* is crystalline, moderately soluble in water, and precipitated from the aqueous solution by alcohol.

Perkin & Duppa.					
4 C .....	24·0	...	9·46	.....	9·81
2 H .....	2·0	...	0·78	.....	0·82
I .....	127·0	...	50·05	.....	49·63
Ba .....	68·6	...	27·06	.....	26·90
4 O .....	32·0	...	12·65	.....	12·84
<hr/>					
C <sup>4</sup> H <sup>3</sup> IBaO <sup>4</sup> .....	253·6	...	100·00	.....	100·00

The *lead-salt* crystallizes in prisms, but is difficult to obtain pure, as it easily splits up into iodide of lead and glycolic acid. Its aqueous solution decomposed by sulphuretted hydrogen, yields hydriodic and glycolic acids.

*Iodacetate of Ethyl* is an oily liquid, heavier than water, and having

a very irritating odour. *Iodacetate of amyl* is also oily and heavier than water. It has the odour of pears, and when heated, gives off a vapour which irritates the eyes and nose.

Page 187.

### Bibromacetic Acid. $C^4H^2Br^2O^4$ .

PERKIN & DUPPA. *Chem. Soc. Qu. J.* 12, 1; *Ann. Pharm.* 110, 115.

Formed, together with monobromacetic acid, when a mixture of bromine and acetic acid is exposed to light (xii, 535). To obtain it in quantity, monobromacetic acid is exposed to the action of bromine-vapour in strong sunshine. Hydrobromic acid is then evolved, and bibromacetic acid is formed; the product may be freed from hydrobromic acid by passing a stream of dry carbonic acid gas through it at  $120^\circ$ .

Colourless inodorous liquid of sp. gr. 2.25. It was once, during very cold weather, obtained in fine needle-shaped crystals. When placed on the skin, it produces painful blisters like burns. It boils between  $225^\circ$  and  $230^\circ$ , but cannot be distilled without decomposition.

*Bibromacetate of Ammonia.*  $C^4H(NH^4)Br^2O^4 + Aq.$  — Obtained by neutralizing the acid with ammonia, and leaving the solution to evaporate, either in the air or over oil of vitriol in vacuo. Forms splendid crystals, which give off their water of crystallization at  $100^\circ$ , becoming at the same time white and opaque. It gave by analysis 6.20 p. c. nitrogen, the formula requiring 5.95 p. c. Heated to  $100^\circ$  with excess of ammonia, it is decomposed, turning brown and giving off volatile products, the nature of which has not yet been determined. It dissolves readily in water, alcohol, and ether.

The *potash-salt* forms long, highly lustrous needles, containing water of crystallization, and very soluble in water and alcohol.

The *lead-salt* is uncrystallizable, very soluble in water, and precipitated in white flocks by alcohol.

The *mercuric-salt* is obtained in the crystalline state by adding mercurous nitrate to bibromacetic acid. It decomposes at  $100^\circ$ , like the silver-salt.

The *silver-salt*, obtained by adding nitrate of silver to the aqueous acid, crystallizes in microscopic needles.

						Perkin & Duppa.	
4 C .....	24	....	7.38	.....	....	7.50	
H .....	1	....	0.30	.....	....	0.48	
Ag .....	108	....	33.23	.....	33.00	33.41	33.37
2 Br .....	160	....	49.23	.....	49.26	48.75	49.02
4 O .....	32	....	9.86	.....			
$C^4HAgBr^2O^4$ .....						325	100.00

It decomposes at  $100^\circ$ , in contact with water, yielding bromide of silver and *bromoglycolic acid*:



The silver-salt of bromoglycolic acid heated in presence of water, yields bromide of silver and an acid having the composition  $C^4H^4O^3$ .



*Bibromacetate of Ethyl*,  $C^4H(C^4H^5)Br^2O^4$ ; is easily obtained by heating an alcoholic solution of the acid in a sealed tube for an hour or two. On treating the contents of the tube with water, the ether separates as a heavy oil, which must be repeatedly washed with water, and then dried over oil of vitriol in vacuo; this treatment does not however, quite remove the free acid. It has a burning taste and attacks the eyes strongly. It is for the most part decomposed by distillation; also by contact with chloride of calcium. It gave by analysis 19.43 p. c. carbon, and 2.33 hydrogen, the formula requiring 19.51 C, and 2.50 H.

*Bibromacetate of Amyl*, obtained like the ethyl-compound, is a heavy oil, having an aromatic odour like that of acetate of amyl.

*Bibromacetamide*.  $C^4H^3Br^2NO^3 = N, H^2, C^4HBr^2O^3$ . — Produced by the action of ammonia on bibromacetate of ethyl:



					Perkin & Duppa.	
4 C .....	24	...	11.05	.....	...	11.53
3 H .....	3	...	1.38	.....	...	1.49
2 Br .....	160	...	73.73	.....	...	73.97
N .....	14	...	6.45	.....	6.84	.... 6.55
2 O .....	16	...	7.37			
<hr/>						
$C^4H^3Br^2NO^3$ .....	217	...	100.00			

### Bromide of Bromethylene. $C^4H^3Br, Br^2$ .

When bromethylene (the so-called bromide of acetyl)  $C^4H^3Br$  (viii, 366), is placed in a long-necked flask, surrounded with a freezing mixture, and bromine added by small portions, combination takes place with great energy, each addition of bromine being attended with a hissing noise. The heavy liquid thus produced is to be washed, first with alkaline, then with pure water, and dried over chloride of calcium. It distils above  $180^\circ$ , in the form of a colourless liquid, which smells like chloroform. The rectified product has a density of 2.620 at  $23^\circ$ , boils at  $186.5^\circ$ , and contains :

					Wurtz.	
4 C .....	24	...	8.59	.....	9.10	
3 H .....	3	...	1.12	.....	1.15	
3 Br .....	240	...	89.89			
<hr/>						
$C^4H^3Br^3$ .....	267	...	100.00			

(Wurtz, *N. Ann. Chim. Phys.* 51, 84.)

Page 191.

Chloracetene.  $C^4H^3Cl$ .T. HARNITZ-HARNITZKY. *Compt. rend.* 48, 649. *Ann. Pharm.* 111, 192.

Produced by the action of phosgene gas on aldehyde:



When phosgene gas is introduced into a vessel containing vapour of aldehyde, an abundant evolution of hydrochloric acid takes place; and if the gaseous products are passed into a receiver which is kept very cold, chloracetene condenses in the form of a liquid which soon solidifies in elongated laminæ. It melts again at  $0^\circ$  and boils at  $45^\circ$ . Vapour-density (determined at  $100^\circ$ ) = 2.1887.

Harnitzky.						Vol.	Density.		
4 C .....	24.0	...	38.46	.....	37.88	C-vapour ....	4	.....	1.6640
3 H .....	3.0	...	4.81	.....	4.85	H-gas ....	3	.....	0.2079
Cl .....	35.5	...	56.73	.....	57.16	Cl-gas ....	1	.....	2.4543
<hr/>									
C <sup>4</sup> H <sup>3</sup> Cl .....	62.5	...	100.00	.....	99.89	Vapour ....	2	.....	4.3262
							1	.....	2.1631

Isomeric or probably identical with the compound which has been variously designated as *chloride of acetyl*, *chloride of acetosyl*, *chloride of acetosum*, *chloride of vinyl*, *chloride of aldehydene*, *chlorethylene*, *chlorethose* (ix, 191). — Its formation from aldehyde by the action of phosgene, tends to show that the rational formula of aldehyde is  $C^4H^3, H, O^2$  rather than  $C^4H^3O^2, H$ .

Chloracetene sinks in water, assumes a buttery consistence, and finally dissolves, with rise of temperature and decomposition, yielding a solution which contains aldehyde and hydrochloric acid:



Heated to  $100^\circ$  in a sealed tube with benzoate of baryta, it forms cinnamic acid, which may be extracted by ether and obtained in crystals by evaporation:



As benzoic acid and cinnamic acid differ by  $C^4H^2$ , it is probable that palmitic acid  $C^{26}H^{52}O^4$  may in like manner be converted into oleic acid  $C^{26}H^{50}O^4$ , and generally, that the acids of the series  $C^{2n}H^{2n}O^4$  may, by the action of chloracetene, be converted into acids of the series  $C^{2n}H^{2n-2}O^4$ , (Harnitzky.)

Page 200.

*Chloral*. From experiments made by Kyburg (*Ann. Pharm.* 106, 253), it appears that chloral exhibits the following reactions analogous to those of aldehyde. — 1. It forms with ammonia a compound which



reduces silver, and from which sulphuretted hydrogen throws down a sulphur compound probably allied to thialdine (ix, 313). — 2. Its aqueous solution yields, with sulphuretted hydrogen, a compound analogous to ordinary mercaptan. — 3. It forms crystalline compounds with the bisulphites of soda and ammonia. — 4. With hydrocyanic acid and hydrochloric acid, it yields an acid resembling lactic acid.

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Page 207.

**Chloralide.**  $C^{10}H^2Cl^6O^6$ . — According to Kekulé (*Ann. Pharm.* 105, 293), chloralide is obtained in greatest abundance by heating chloral which has been once distilled over ordinary oil of vitriol, with fuming sulphuric acid, till sulphurous acid begins to appear amongst the gaseous products of decomposition (hydrochloric acid and carbonic oxide):



As the liquid cools, the oily layer which floats on the sulphuric acid, solidifies in crystals, which by recrystallization from alcohol yield pure chloralide.

						Kekulé.
10 C	.....	60	...	18.58	.....	18.64
2 H	.....	2	...	0.62	.....	0.72
6 Cl	.....	213	...	65.94	.....	65.84
6 O	.....	48	...	14.86	.....	66.15
<hr/>						
$C^{10}H^2Cl^6O^6$	.....	323	...	100.00		

The analysis agrees better, on the whole, with the formula above given (Städeler's), than with Gmelin's formula  $C^8H^2Cl^5O^5$ , requiring 17.98 C, 0.75 H, and 66.29 Cl, or with Gerhardt's,  $C^{12}H^3Cl^7O^8$ , which requires 18.58 C, 0.77 H, and 64.13 Cl.

According to Städeler, the first product of the action of sulphuric acid upon chloral, is insoluble chloral ( $C^4HCl^3O^2$ ); and this compound is afterwards resolved into chloralide and chloroform,  $C^2HCl^3$  (or its products of decomposition, hydrochloric acid and chloride of carbon), according to the equation:



The evolution of carbonic oxide observed by Kekulé in the preparation of chloralide, is regarded by Städeler as proceeding from a secondary decomposition of chloral into carbonic oxide and chloroform or its products of decomposition.

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Page 237.

**Action of Chlorine on Acetic Ether.** — According to Schillerup (*Ann. Pharm.* 111 129), when chlorine is passed to saturation through acetic ether (boiling at 74°) in the shade, first at the atmospheric temperature and afterwards at 100°, the chief products obtained are mono-, bi-, and ter-chlorinated acetic ether, which however cannot be separated by fractional distillation. If the acetic ether contains alcohol, bichloroacetal and terchloroacetal are likewise formed (p. 477).

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Page 246.

*Acetamide*,  $C^4H^5NO^2$ , may be obtained by heating an intimate mixture of 1 At. fused acetate of soda and 1 At. sal-ammoniac:



The mixture fuses and soon gives off a thick oily liquid, which solidifies in the neck of the retort and in the receiver, and when freed from water by evaporation and rectified, yields pure acetamide. Nitrogen by analysis 23.7 p. c. by calculation 23.9.

A mixture of benzoate of soda and chloride of ammonium similarly treated yields benzamide.

The iodides of tetrethylum and tetramethylum heated with acetate of soda, do not yield the compound amides  $C^2(H^4Et)NO^2$  and  $C^2(H^3Me)NO^2$ . With iodide of tetrethylum the decomposition is:



(Petersen, *Ann Pharm.* 107, 331.)

*Hydrochlorate of Acediamine*,  $C^4H^5N^2.HCl$  (xii, 546), which is obtained in great abundance by heating hydrochlorate of acetamide in a stream of dry hydrochloric acid gas,—is resolved by the action of nitrite of silver, into acetate of ammonia and free nitrogen. (Petersen, *loc. cit.*)

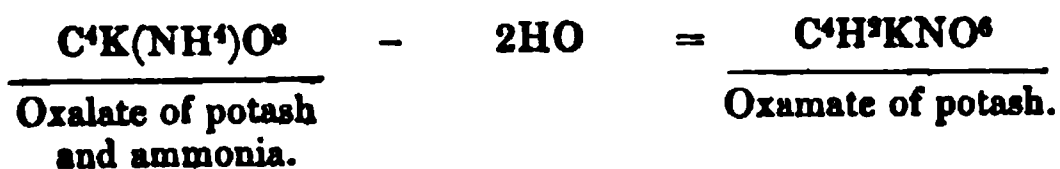


Page 259.

## Oxamic Acid.

P. J. ENGSTRÖM. *J. pr. Chem.* 68, 433.

The potash-salt of this acid may be prepared by heating crystallized oxalate of potash and ammonia to  $230^\circ$ , till the mass which softens at first, again becomes solid:



The brownish aqueous solution of the residue treated with chloride of barium, yields a precipitate of oxamate of baryta; and by dissolving this precipitate in boiling water (any undecomposed oxalic acid then remaining undissolved as oxalate of baryta), and decomposing the solution with various soluble sulphates, the corresponding salts of oxamic acid are obtained.

*Oxamate of Ammonia*,  $C^4H^2(NH^4)NO^6$ , crystallizes from a hot solution in anhydrous prisms; from a cold solution in granules consisting of  $C^4H^2(NH^4)NO^6 + 3Aq$ . A salt with 2 At. water appears also to exist. — The anhydrous salt crystallizes according to Sénarmont (*Jahresber. d. Chem.* 1857, 296) in prisms belonging to the oblique prismatic (monoclinometric) system,  $\infty P . (\infty P2) . \infty P \infty . P \infty . oP$ . The clinodiagonal is to the orthodiagonal as  $0.6489 : 1$ . Inclination of the clinodiagonal to the principal axis =  $64^\circ 23'$ ;  $\infty P : \infty P$  in the principal section of the clinodiagonal =  $119^\circ 20'$ ;  $(\infty P2) : (\infty P2)$  in the same section =  $81^\circ 2'$ ;  $oP : \infty P = 111^\circ 55'$ .

*Oxamate of Potash* separates from concentrated solutions in long silky needles  $C^4H^2KNO^6 + 2Aq$ . which give off their water at  $100^\circ$ , are very soluble in water, less soluble in alcohol.

*Oxamate of Soda* was obtained in groups of microscopic prisms which effloresced readily, and after pressure between paper, exhibited the composition  $C^4H^2NaNO^6 + Aq$  (7.5 p. c. water). When crystallized from concentrated solutions however, it contained only 2.3 p. c. water; by spontaneous evaporation, it crystallized with 10.8 p. c. water corresponding to the formula  $2C^4H^2NaNO^6 + 3Aq$ .

*Oxamate of Baryta* forms four-sided prisms  $C^4H^2BaNO^6 + 3Aq$ , which are permanent at ordinary temperatures, but give off their water at  $210^\circ$ . The anhydrous salt dissolves in 537 pts. of water at  $13^\circ$  and in 25.6 pts. at  $100^\circ$ .

*Oxamate of Lime* forms microscopic quadratic prisms  $C^4H^2CaNO^6 + 4Aq$  which give off nearly all their water at  $100^\circ$ . The anhydrous salt dissolves in 638 pts. of water at  $13^\circ$  and in 24.6 pts. of boiling water.

*Oxamate of Magnesia*,  $C^4H^2MgNO^6 + 3Aq$ , forms small granules composed of slender needles, which dissolve in 54.7 pts. of water at  $14^\circ$ , and in 4.98 pts. of boiling water.

*Oxamide*. — Oxamide mixed with 10 times its weight of dehydrated *glycerin* remains unaltered when heated to  $100^\circ - 120^\circ$ , but at about  $180^\circ$  it yields a sublimate of pure carbonate of ammonia. — When heated by itself, it sustains a heat of  $180^\circ$  without decomposition. — Heated with *anhydrous phosphoric acid*, it gives off cyanogen gas together with carbonic acid and carbonic oxide. With a mixture of 1 pt. oxamide and 8 pts. or more of phosphoric anhydride, the decomposition is attended with blackening and intumescence. The evolution of gas begins between  $120^\circ$  and  $130^\circ$ , and is tolerably brisk and regular between  $150^\circ$

and 160°. With 8 pts. phosphoric anhydride, the gaseous mixture consists of 82.7 vol. cyanogen, 6.1 vol. carbonic oxide and 11.2 vol. carbonic acid; with 16 pts. of phosphoric anhydride, the gaseous mixture contains 71.2 vol. C<sup>2</sup>N, 9.1 CO and 19.7 CO<sup>2</sup>. — When 1 pt. oxamide is heated with 12 pts. of fused and pulverized *chloride of zinc*, the action begins between 260° and 270°; and the mixture melts and gives off a gas containing 75.5 vol. CO<sup>2</sup> to 22.9 vol. CO and 1.6 vol. C<sup>2</sup>N. (Bertagnini, *Cimento* 5, 55; *Ann. Pharm.* 104, 175.)

Oxamide heated with absolute alcohol to 210° — 220° for several days in a sealed tube, is gradually converted into solid crystals, having the form of rectangular prisms, with octohedral bevelling, oblique striation, and octohedral cleavage. Neither oxalic acid nor oxamethylene is produced, but ammonia is eliminated and probably oxalate of ethyl is formed. (Geuther.)

Oxamide is sparingly soluble in boiling water, and the solubility is increased by the addition of chloride of calcium or neutral oxalate of potash. The solution when gradually cooled, deposits pure oxamide in long, interlaced needles. (A. Geuther, *Ann. Pharm.* 109, 72.)

Page 274.

*Urethane.* — According to Cloez (*Ann. Pharm.* 104, 32), alcohol which has been several times used for the recrystallization of crude cyanate of potash, contains urethane. A quantity of this alcoholic mother-liquor, after being freed by distillation from the volatile portion, separated into two layers, the lower of which was a solution of sesquicarbonate of potash, while the upper yielded, on cooling, crystals of urethane. To explain the formation of urethane under these circumstances, Cloez supposes that ammonia and bicarbonate of potash are first produced by the action of the aqueous alcohol on the cyanate of potash; that, when the liquid is heated, the bicarbonate gives up carbonic acid, which at the moment of liberation forms carbonate of ethyl; and that this ether is converted into urethane (carbamate of ethyl) by the ammonia. Experiments made to ascertain whether carbonic ether is produced by heating bicarbonate of potash with alcohol in sealed tubes yielded no result, as the tubes always burst.

Urethane is also produced, together with chloride of ammonium, when a solution of chloride of cyanogen in anhydrous ether is left to itself for a month at ordinary temperatures. (Cloez.)

Page 291.

*Biethyl-urea.*  $C^{10}N^2H^{12}O^3 = C^2N^2H^2(C^4H^5)^2O^3 = N^2(C^2O^2)^2H^2(C^4H^5)^2$ . — This compound is formed, together with cyanate of ethyl, by the dry distillation of the oily body  $C^{16}H^{17}N^3O^4$ , produced by boiling cyanurate of ethyl with baryta-water (p. ).



After repeated distillation and crystallization from anhydrous ether, it forms long prisms which melt at 106° and distil without decomposition at about 250°.

					Habich & Limpricht.	
10 C	.....	60	...	51.7	.....	51.3
12 H	.....	12	...	10.3	.....	10.5
2 N	.....	28	...	24.1		
2 O	.....	16	...	13.9		
<hr/>						
C <sup>10</sup> H <sup>12</sup> N <sup>2</sup> O <sup>2</sup>	.....	116	...	100.0		

Heated with potash-ley or hydrate of lime, it is resolved into carbonic acid and ethylamine :



In dry hydrochloric acid gas, it changes into a viscid mass, which is resolved by distillation into hydrochlorate of ethylamine, and hydrochlorate of cyanic ether (propionitrile):



The same products are obtained, together with others, by the action of chlorine on biethyl-urea. (Habich & Limpricht, *Ann. Pharm.* 109, 165.)

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Page 363.

### Allyl-compounds.

BERTHELOT & DE LUCA. *N. Ann. Chim. Phys.* 43, 257; 44, 495; 48, 286; abstr. *Compt. rend.* 42, 233.

ZININ. *Ann. Pharm.* 95, 128; 96, 361.

CAHOURS & HOFMANN. *Phil. Trans.*, 1857, 555; *Ann. Pharm.* 102, 285; abstr. *Proc. Roy. Soc.* 8, 511; *Chem. Soc. Qu. J.* 10, 316.

*Allyl.* C<sup>3</sup>H<sup>4</sup> = C<sup>2</sup>H<sup>3</sup>,C<sup>1</sup>H<sup>1</sup>. — Obtained by the action of sodium on iodide of allyl (iodopropylene) or on bibromide of allyl. — 100 grammes of the iodide and 40 or 50 grammes of sodium well purified from rock-oil, are gently heated for about 2 hours in a small flask provided with a condensing tube, so that the liquid which volatilizes may flow back again, and the product is then distilled, whereupon allyl condenses in the receiver to the amount of 15 or 20 grammes. On redistilling the product nearly the whole passes over at 59°. Care must be taken in the first distillation not to allow the heat to rise too high, because the sodium then unites with the organic matter, forming a compound which is easily destroyed by heat. (Berthelot & De Luca.)

Allyl is a very volatile liquid having a peculiar, ethereal, penetrating odour, like that of horse-radish. Sp. gr. 0.684 at 14°. Boiling point 59°. Vapour-density 2.92. Burns with a very bright flame.

B. & L.						Vol.	Density.
12 C .....	72	....	87.8	.....	87.2	C-vapour .....	12 .... 4.9920
10 H .....	10	....	12.2	.....	19.2	H-gas .....	10 .... 6.6930
$C^{12}H^{10}$ .....	82	....	100.0	.....	99.7	Allyl-vapour.....	2 .... 5.6850
							1 .... 2.8925

Allyl mixes with *oil of vitriol*, producing considerable rise of temperature; if however the mixture be kept cool, the mass scarcely becomes coloured, but after some hours, a considerable portion of the hydrocarbon floats on the surface. — Fuming *nitric acid* changes allyl into a liquid neutral nitro-compound, soluble in ether, and decomposed by heat. — *Hydrochloric acid* gas is not sensibly absorbed by allyl, even after several days. — With *chlorine*, it gives off hydrochloric acid and forms a liquid heavier than water.

Allyl unites readily with *iodine* and *bromine*, forming the compounds  $C^6H^5I^2$  and  $C^6H^5Br^2$ . (Berthelot & De Luca.)

*Oxide of Allyl.*  $C^6H^5O$  or rather  $(C^6H^5)^2O^2$ . — *Allylic Ether.* — Exists in small quantity in oil of garlic (ix, 363). — Produced by the action of iodide of allyl on allylate of potassium:



also by the action of iodide of allyl on mercuric oxide or silver-oxide:

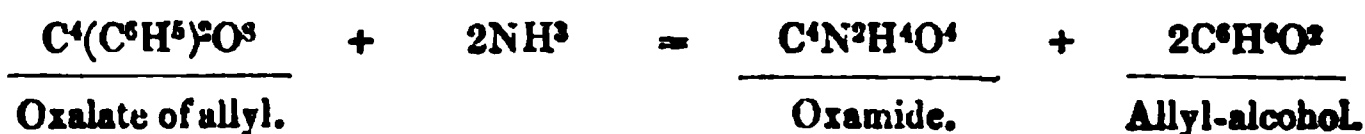


It is a colourless, mobile, very volatile liquid, lighter than water, and insoluble therein, and bears considerable resemblance to common ether. Boils at 82° (Cahours & Hofmann); between 85° and 87°. (Berthelot & De Luca.) — With oil of vitriol, it forms an acid the baryta-salt of which is soluble: if however the liquids be too quickly mixed, carbonization takes place attended with explosion. — Nitric acid converts the ether into a nitro-compound, heavier than water. Iodide of phosphorus converts it into iodide of allyl. Heated with butyric acid to 250°, it yields a small quantity of butyrate of allyl. (Berthelot & De Luca.)

*Ethyl-allyl-ether*,  $C^4H^5, C^6H^5, O^2$ , is produced in like manner by treating allylate of potassium with iodide of ethyl, or ethylate of potassium with iodide of allyl. It is a colourless aromatic liquid boiling at 64°. (Cahours & Hofmann.)

Similarly, by treating iodide of allyl with methylete, amylete and phenylete of potassium, the compounds  $\left. \begin{matrix} C^6H^5 \\ C^3H_3 \end{matrix} \right\} O^2$ , &c., are produced. (Cahours & Hofmann.)

**Allyl-alcohol.**  $C^3H^5O^2 = C^3H^5, H, O^2$ . *Hydrate of Allyl, Hydrated Oxide of allyl.* — Produced by the action of ammonia on oxalate of allyl, oxamide being formed at the same time. (Cahours & Hofmann.)



Apparently also by distilling benzoate or acetate of allyl with potash. (Zinin, *Ann. Pharm.* 96, 362). — To prepare it, dry ammonia gas is passed into oxalate of allyl, whereupon the whole solidifies to a mass of oxamide containing the alcohol mechanically enclosed. The alcohol may then be separated by distillation, and freed from traces of ammonia and water by rectification over dry sulphate of copper.

**Properties.** Colourless mobile liquid, having a peculiar, pungent, but not unpleasant odour, slightly resembling the odours of common alcohol and oil of mustard. Its taste is spirituous and burning. Boils at  $103^\circ$  (or according to another determination by Hofmann, at  $93^\circ$ ; but the former agrees best with the differences generally observed between corresponding ethyl- and allyl-compounds). It is very inflammable and burns with a brighter flame than common alcohol.

Cahours & Hofmann.					
6 C	.....	36	....	62.07	..... 62.08
6 H	.....	6	....	10.34	..... 10.43
2 O	.....	16	....	27.59	..... 27.49
<hr/>					
$C^3H^5O^2$	.....	58	....	100.00	..... 100.00

Isomeric with acetone and propylic aldehyde.

**Decompositions.** 1. Allyl-alcohol is easily altered by *oxidizing agents*. A mixture of sulphuric acid and chromate of potash, rapidly converts it into acroleine and acrylic acid (ix, 365, 369). — The same change is produced by the agency of platinum-black. — 2. *Anhydrous* phosphoric acid strongly attacks allyl-alcohol at a gentle heat, eliminating a colourless inflammable gas, probably  $C^3H^4$ . — 3. *Oil of vitriol* converts allyl-alcohol into allyl-sulphuric acid, which forms soluble and crystallizable salts with baryta, strontia, and oxide of lead. — 4. With *potash* and *bisulphide of carbon*, it forms allylxanthate of potassium, which crystallizes in beautiful yellow needles. — 5. Distilled with *chloride, bromide, or iodide of phosphorus*, it yields chloride, bromide, or iodide of allyl. — 6. *Potassium* decomposes it, eliminating hydrogen and forming allylate of potassium,  $C^3H^5KO^2$ . (Cahours & Hofmann.)

**Combinations.** Allyl-alcohol mixes in all proportions with water, common alcohol, and common ether. (Cahours & Hofmann).

**Sulphide of Allyl.**  $C^{12}H^8S^2 = (C^3H^5)^2S^2$ . — Constitutes the essential part of volatile oil of garlic (ix, 372). — Produced artificially by cautiously dropping iodide of allyl into a concentrated alcoholic solution of monosulphide of potassium. The liquid becomes very hot, and yields an abundant crystalline deposit of iodide of potassium. As soon as the action

is over, a slight excess of sulphide of potassium is to be added, and the whole mixed with water. Sulphide of allyl then rises to the surface, as a light, transparent, yellowish oil, possessing in a high degree the odour of garlic-oil. By rectification it becomes colourless, and then boils at  $140^{\circ}$ .

Cahours & Hofmann.					
12 C	.....	72	...	63.16	..... 63.3
10 H	.....	10	...	8.78	..... 8.9
2 S	.....	32	...	28.06	
<hr/>					
$C^{12}H^{10}S^2$	.....	98	...	100.00	

Artificial sulphide of allyl forms compounds with nitrate of silver, chloride of mercury, and bichloride of platinum, exactly like those produced by the natural oil. (Cahours & Hofmann).

*Allyl-mercaptan.*  $C^6H^8S^2 = C^6H^5, H; S^2$ . — *Sulphide of Allyl and Hydrogen, Hydrosulphate of Allyl, Sulphydrate of Allyl.* — Produced by the action of iodide of allyl on sulphydrate of potassium:



It is a volatile oily liquid, having an odour like that of the preceding compound, but more ethereal. Bears considerable resemblance to ethyl-mercaptan. Boils at  $90^{\circ}$ .

Cahours & Hofmann.					
6 C	.....	36	...	48.65	..... 48.86 ... 48.71
6 H	.....	6	...	8.11	..... 8.23 ... 8.30
2 S	.....	32	...	43.24	
<hr/>					
$C^6H^8S^2$	.....	74	...	100.00	

Allylmercaptan acts energetically on mercuric oxide, forming a compound ( $C^6H^8HgS^2$ ), which dissolves in boiling alcohol, and separates on cooling, in scales having a strong mother-of-pearl lustre. (Cahours & Hofmann.)

*Iodide of Allyl.*  $C^6H^5I$ . — *Allylhydriodic ether, Iodopropylene.* — Produced by the action of biniodide of phosphorus on glycerin. (Berthelot & De Luca, see ix, 427.)

*Biniodide of Allyl.*  $C^6H^5I^2$ . Obtained by dissolving 6 or 7 pts. of iodine in 1 pt. of allyl gently heated. The mixture liquefies at first, but in a few minutes becomes solid; it is then triturated with aqueous potash, to remove the excess of iodine, and crystallized from boiling ether. — It is colourless when first prepared, but is rapidly coloured by exposure to light. Smells like iodide of ethylene.

Berthelot & De Luca.					
6 C	.....	36	...	12.2	..... 12.3
5 H	.....	5	...	1.7	..... 1.7
2 I	.....	252	...	86.1	..... 85.5
<hr/>					
$C^6H^5I^2$	.....	293	...	100.0	..... 99.5



This compound melts at a temperature above  $100^{\circ}$ , forming a heavy liquid, which is decomposed by a stronger heat, yielding iodine, carbonaceous matter, and a very heavy, neutral, volatile liquid, insoluble in potash. (This liquid is not  $C^6H^5I$ : for, when treated with mercury and hydrochloric acid, it does not yield propylene [ix, 427]. — Biniodide of allyl is decomposed when heated with sodium, but does not yield definite products, perhaps in consequence of the high temperature required to melt it. — It is but very slightly decomposed by aqueous potash, but alcoholic potash decomposes it readily, when heated with it, forming a product which smells like allyl. — Biniodide of allyl, heated with a mixture of fuming hydrochloric acid and mercury, is but very slightly attacked, and does not give off any appreciable quantity of gas, whereas the compound  $C^6H^5I$ , yields when thus treated, abundance of propylene gas. From these differences of action, Berthelot & De Luca infer that the body  $C^6H^5I$ , does not contain the same radical as  $C^6H^5I^2$ ; further, that since the latter can be produced by the direct union of iodine and allyl, whereas the former cannot,  $C^6H^5I^2$  is the true iodide of allyl, while  $C^6H^5I$ , is a body of totally different molecular constitution. It does not appear possible to produce either of these compounds directly from the other. The body left when  $C^6H^5I^2$  is decomposed by heat, is not identical with iodopropylene (vid. sup.), and on the other hand, iodopropylene is capable of dissolving a considerable quantity of free iodine; but the iodine thus dissolved is easily removed by the action of cold potash. (Berthelot & De Luca.) — Notwithstanding these circumstances, however, it is certain that the compound  $C^6H^5I$  is related to oxalate of allyl and allylic alcohol, in the same manner as  $C^4H^5I$  (iodide of ethyl) is related to oxalate of ethyl and ethylic alcohol, the series of processes by which each of these iodides is converted into the corresponding alcohol, being indeed exactly analogous.

*Bibromide of Allyl.*  $C^6H^5Br^2$ . — Bromine unites with allyl, producing considerable evolution of heat; and if the action be moderated by cooling and the potash added as soon as the liquid begins to exhibit the colour of bromine and give off hydrobromic acid, the liquid soon solidifies in a crystalline mass; and if this mass be strongly pressed, then dissolved in ether, and the solution left to evaporate, crystals of bibromide of allyl are obtained, which may be purified by compression and recrystallization from ether. — They are white, and have an odour like that of bibromide of ethylene, but fainter. The compound is very soluble in ether, but insoluble in water. It melts at  $37^{\circ}$ , and if the fusion is incomplete, solidifies at the same temperature; but if completely melted, it does not resume the solid state till cooled several degrees lower. It may even remain liquid at  $6^{\circ}$ , and exhibits considerable rise of temperature at the moment of solidification. — It is volatile without decomposition. — Heated with sodium, it is decomposed and yields allyl. (Berthelot & De Luca.)

Berthelot & De Luca.					
6 C	.....	36	...	17.9	..... 18.4
5 H	.....	5	...	2.5	..... 2.4
2 Br	.....	160	...	79.6	..... 78.9
<hr/>					
$C^6H^5Br^2$	.....	201	...	100.0	..... 99.7

*Terbromide of Allyl.*  $C^6H^5Br^3$ . — Obtained by gradually adding 3 pts. of bromine to 2 pts. of iodide of allyl,  $C^6H^5I$ , cooled in a freezing mixture; leaving the liquid to stand till the next day; then washing the liquid separated from crystallized iodine with alkaline and afterwards with pure water; dehydrating; distilling (whereupon it turns brown, and gives off iodine-vapours); again washing and distilling that which has

passed over; collecting apart that which distils between  $210^{\circ}$  and  $220^{\circ}$ ; cooling the purple-red liquid thus obtained to  $0^{\circ}$ , whereupon it solidifies in the crystalline state; removing the red mother-liquor; and lastly, fusing and again rectifying the product. (A. Wurtz, *N. Ann. Chim. Phys.* 51, 91.)

Colourless neutral liquid, having a not unpleasant odour. Sp. gr. 2.436 at  $23^{\circ}$ . Solidifies below  $10^{\circ}$  (by slow cooling, it yields shining prisms which melt at  $16^{\circ}$ ). Boils between  $217^{\circ}$  and  $218^{\circ}$ . Alcoholic potash converts it into an ethereal liquid which boils at about  $135^{\circ}$ . — (Wurtz.)

						Wurtz.
6 C	.....	36	....	12.81	.....	13.11 .... 13.05
5 H	.....	5	....	1.78	.....	1.85 .... 1.65
3 Br	.....	240	....	85.41	.....	84.34
<hr/>						
$C^6H^5Br^3$	.....	281	....	100.00		

This compound, called *isotribromhydrin* by Berthelot and De Luca, is isomeric with *terbromhydrin* obtained by the action of  $PBr^5$  on *bibromhydrin* or *epibromhydrin* and with *bibromide of bromopropylene* (p. 552). — From the former it differs by its boiling point; from the latter by its boiling point and specific gravity, by solidifying above  $0^{\circ}$ , and by its behaviour with alcoholic potash, with ammonia, with oxide of silver, and with sodium.

*Terbromide of allyl* is converted by *alcoholic potash* into an ethereal liquid, which boils at  $135^{\circ}$ . (Wurtz.) — *Ammonia* converts it into *bibromallylamine*,  $N(C^6H^4Br)^3, H$ , and *bromide of ammonium* (Simpson, p. 549); *bromide of bromopropylene*, on the other hand is converted by *ammonia* into *bromide of ammonium* and the compound  $C^{12}H^8Br^6 = C^6H^4Br^2, C^6H^4Br^2$ . (Simpson, p. 552). With moist *oxide of silver*, it yields *bromide of silver* and *glycerine*:



*Bromide of bromopropylene* treated with *silver-salts* does not reproduce *glycerine*. (Berthelot and De Luca, *N. Ann. Chim. Phys.* 52, 441). — *Terbromide of allyl* is decomposed by *sodium*, yielding *allyl* and *bromide of sodium*, but it is difficult to remove the whole of the bromine. — *Bromide of bromopropylene* treated with *sodium*, yields, not *allyl*, but *bibromopropylene*,  $C^6H^4Br^2$ . (Berthelot & De Luca.)

*Carbonate of Allyl*.  $CO^2, C^6H^5$ , is obtained by the action of *sodium* on *oxalate of allyl*, *carbonic oxide* being evolved at the same time [ $C^6O^2, (C^6H^5)^2 - 2CO = 2(CO^2, C^6H^5)$ ]. It is a colourless oil, lighter than water, and having an aromatic odour. (Cahours & Hofmann.) It is also produced by the action of *iodide of allyl* on *carbonate of silver*. (Zinin.)

*Allylsulphuric Acid*.  $C^6H^5S^2O^3 = C^6H^5, H, S^2O^3$ . — *Sulphate of Allyl and Hydrogen*. — *Sulphallylic Acid*. — When *allylic alcohol* is added by drops to about an equal volume of strong *sulphuric acid*, the mixture becomes heated without blackening; and on adding 7 or 8 times the

volume of water, and neutralizing with carbonate of baryta, the liquid yields by evaporation white shining crystals of allylsulphate of baryta. (Cahours and Hofmann.)

[Cahours & Hoffmann.

6 C	.....	36	....	17.54	
5 H	.....	5	....	2.43	
Ba	.....	68.5	....	33.33	..... 33.11
2 S	.....	32	....	15.55	
8 O	.....	64	....	31.15	
<hr/>					
C <sup>6</sup> H <sup>5</sup> BaS <sup>2</sup> O <sup>3</sup>	.....	205.5	....	100.00	

*Allylxanthic Acid.* — Allylic alcohol mixed with potash-solution and bisulphide of carbon, yields a body which crystallizes in yellow needles, closely resembling those of xanthate of potash. (Cahours and Hofmann.)

*Cyanate of Allyl.* C<sup>2</sup>N(C<sup>6</sup>H<sup>5</sup>)O<sup>2</sup>. — Produced by the action of iodide of allyl on cyanate of silver. The heat produced by the reaction is sufficient to distil over nearly the whole of the volatile product.  
Transparent colourless liquid having a pungent odour like that of cyanate of ethyl, and intensely tear-exciting. Boils at 82°. Vapour-density 3.045. (Cahours & Hofmann.)

C. & H.					Vol.		Density.
8 C	.....	48	....	57.83	.....	57.75	C-vapour .... 8 ..... 3.3280
5 H	.....	5	....	6.02	.....	6.13	H-gas .... 5 ..... 0.3465
N	.....	14	....	16.86	.....	16.71	N-gas .... 1 ..... 0.9706
2 O	.....	16	....	19.29	.....	19.41	O-gas .... 1 ..... 1.1090
<hr/>							
C <sup>6</sup> H <sup>5</sup> NO <sup>2</sup>	....	73	....	100.00	.....	100.00	2 ..... 5.7544
							1 ..... 2.8772

Cyanate of allyl dissolves readily in ammonia, with evolution of heat, and the solution when evaporated, yields crystals of *allyl-urea*. With ethylamine, it forms in like manner, *ethyl-allyl-urea*. Distilled with potash, it yields *allylamine*. (Cahours & Hofmann.)

*Sulphocyanide of Allyl.* C<sup>3</sup>N(C<sup>6</sup>H<sup>5</sup>)S<sup>2</sup>. — Volatile oil of mustard. — Produced artificially by the action of iodide of allyl on sulphocyanide of potassium or sulphocyanide of silver (x, 42).

*Acetate of Allyl.* C<sup>10</sup>H<sup>8</sup>O<sup>4</sup> = C<sup>4</sup>H<sup>3</sup>(C<sup>6</sup>H<sup>5</sup>)O<sup>4</sup>. — Obtained by distilling acetate of silver with iodide of allyl, and rectifying several times over acetate of silver. — Colourless liquid, lighter than water, and nearly insoluble therein, but miscible with alcohol and ether. It has a pungent aromatic odour, and boils between 98° and 100°. (Cahours & Hofmann.) At 105°. (Zinin.) Boiled with potash, it yields acetate of potash and allylic alcohol. (Cahours & Hofmann.)

Cahours & Hofmann.					Zinin.		
10 C	.....	60	....	60.00	.....	59.87	..... 59.66 .... 60.00
8 H	.....	8	....	8.24	.....	8.09	..... 8.21 .... 8.29
4 O	.....	32	....	31.76	.....	32.04	..... 32.13 .... 31.71
<hr/>							
C <sup>10</sup> H <sup>8</sup> O <sup>4</sup>	.....	100	....	100.00	.....	100.00	..... 100.00 .... 100.00

*Butyrate of Allyl.*  $C^{14}H^{12}O^4 = C^8H^7(C^6H^5)O^4$ . — By distilling butyrate of silver with iodide of allyl, an amber-coloured liquid is obtained, which is rendered colourless by rectification. It is oily, lighter than water, smells like butyrate of ethyl, and boils at about  $140^\circ$ . (Cahours & Hofmann.) About  $145^\circ$ . (Butlerow & Lenssen.) Heated with potash, it yields allylic alcohol and butyrate of potash. It is soluble in ether.

Cahours & Hofmann.					
14 C .....	84	...	65.62	.....	65.86
12 H .....	12	...	9.38	.....	9.58
4 O .....	32	...	25.00	.....	24.56
<hr/>					
$C^{14}H^{12}O^4$ ....	128	...	100.00	.....	100.00

*Valerate of Allyl.*  $C^{16}H^{14}O^4 = C^{10}H^9(C^6H^5)O^4$ . — Prepared like the preceding compound; purified by rectification over valerate of silver, washing with alkaline water, and digestion with chloride of calcium. — It is a colourless liquid, having an aromatic odour like that of valerate of ethyl, lighter than water and insoluble therein, but readily soluble in alcohol and ether. Boils at  $162^\circ$ . Its vapour burns with a bright flame.

Cahours & Hofmann.					
16 C .....	96	...	67.60	.....	67.40
14 H .....	14	...	9.86	.....	10.12
4 O .....	32	...	22.54	.....	22.48
<hr/>					
$C^{16}H^{14}O^4$ .....	142	...	100.00	.....	100.00

*Benzoate of Allyl.*  $C^{20}H^{10}O^4 = C^{14}H^5(C^6H^5)O^4$ . — Obtained by the action of chloride of benzoyl on allylic alcohol, or of iodide of allyl on benzoate of silver. — Amber-coloured liquid, heavier than water and insoluble therein, but miscible in all proportions with wood-spirit, alcohol, and ether; smells like benzoate of ethyl. Boils at  $228^\circ$ . (Cahours & Hofmann.) At  $242^\circ$ . (Zinin.)

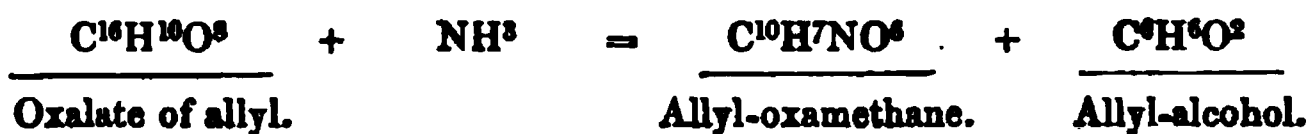
Cahours & Hofmann.						Zinin.
20 C .....	120	...	74.07	.....	73.10	74.29
10 H .....	10	...	6.17	.....	6.24	6.44
4 O .....	32	...	19.76	.....	20.66	19.27
<hr/>						
$C^{20}H^{10}O^4$ .....	162	...	100.00	.....	100.00	100.00

*Oxalate of Allyl.*  $C^{16}H^{10}O^8 = C^4(C^6H^5)_2O^8$ . — Oxalate of silver is digested for several hours at  $100^\circ$ , with iodide of allyl mixed with anhydrous ether, and the product is purified by a single rectification. — Colourless oily liquid, of specific gravity 1.055 at  $15.5^\circ$ . Smells like oxalate of ethyl, but with a slight admixture of the odour of mustard. Boils between  $206^\circ$  and  $207^\circ$  with the barometer at 754<sup>mm</sup>.

Cahours & Hofmann.					
16 C .....	96	...	56.47	.....	56.31
10 H .....	10	...	5.88	.....	5.92
8 O .....	64	...	37.65	.....	37.77
<hr/>					
$C^{16}H^{10}O^8$ .....	170	...	100.00	.....	100.00

Oxalate of allyl is slowly decomposed by water, and instantly by solution of potash. With ammonia, it forms oxamide and allylic alcohol (p. 540).

*Oxamate of Allyl.*  $C^{10}H^7NO^6 = C^4NH^3(C^6H^5)O^6$  — *Allyl-oxamethane*. — Produced on adding oxalate of allyl, drop by drop, to an alcoholic solution of ammonia.



It is soluble in alcohol, and separates from the solution by spontaneous evaporation in splendid crystals.

Cahours & Hofmann.					
10 C .....	60	...	46.51	.....	46.29
7 H .....	7	...	5.42	.....	5.55
N .....	14	...	10.84		
6 O .....	48	...	37.23		
<hr/>					
$C^{10}H^7NO^6$ .....	129	...	100.00		

*Allyl-urea.*  $C^9H^8N^2O^3 = N^2.H^3.C^6H^5.C^3O^3$ . — Obtained by dissolving cyanate of allyl in ammonia; separates by evaporation in the form of a splendidly crystallized mass. — Crystallizes very easily, both from water and from alcohol. (Cahours & Hofmann.)

Cahours & Hofmann.					
8 C .....	48	.....	47.81		
8 H .....	8	.....	8.11		
2 N .....	28	.....	27.86		
2 O .....	16	.....	16.22		
<hr/>					
$C^9H^8N^2O^3$ .....	100	.....	100.00		

The composition is that of thiosinamine (x, 57), in which the sulphur is replaced by an equivalent quantity of oxygen.

*Ethyl-allyl-urea.*  $C^{13}H^{12}N^2O^3 = N^2.H^3(C^4H^5)(C^6H^5).C^3O^3$ . — Produced by the action of ethylamine on cyanate of allyl. Crystallizes in beautiful prisms :

Cahours & Hofmann.					
12 C .....	72	...	56.25	.....	56.12
12 H .....	12	...	9.37	.....	9.25
2 N .....	28	...	21.95		
2 O .....	16	...	12.43		
<hr/>					
$C^{13}H^{12}N^2O^3$ ....	128	...	100.00		

Similar compounds are formed by the action of *methylamine*, *amylamine* and *phenylamine* on cyanate of allyl.

*Biallyl-urea.*  $C^{14}H^{12}N^2O^3 = N^2.H^3(C^6H^5)^2.C^3O^3$ . *Sinapoline*. — Produced : 1. By the action of hydrated oxide of lead on oil of mustard

(x, 39). — 2. By heating cyanate of allyl with water, whereupon it becomes buttery and ultimately solidifies, or with aqueous potash, taking care in this case that the action does not go too far, otherwise the sinapoline disappears entirely and the product consists wholly of amine-bases. The formation is represented by the equation :



The product thus obtained is identical in composition and properties with that which is produced by the action of hydrate of lead and other bases on oil of mustard. (Cahours & Hofmann.)

*Allylamine.*  $\text{C}^3\text{H}^7\text{N} = \text{N}, \text{H}^3, \text{C}^3\text{H}^5$ . — Cyanate of allyl boiled for some time with strong potash-ley is finally converted into carbonic acid and a mixture of volatile bases among which allylamine is found in considerable quantity :



If the evolved vapours are condensed in hydrochloric acid, and the solution mixed with bichloride of platinum, a pale yellow precipitate is formed, variable in quantity and in composition; and the filtrate yields by evaporation, splendid orange-red needles of the platinum-salt of allylamine. — This base is also produced by the action of ammonia on iodide of allyl :

<i>Platinum-salt.</i>				<i>Cahours &amp; Hofmann.</i>	
6 C	.....	37.0	... 13.68	.....	12.61
8 H	.....	8.0	... 3.05	.....	3.07
N	.....	14.0	... 5.31		
3 Cl	.....	106.5	... 40.46		
Pt	.....	98.7	... 37.50	.....	37.43 to 37.62
<hr/>					
$\text{C}^3\text{H}^7\text{N}, \text{HCl}, \text{PtCl}^2$		... 264.2	... 100.00		

*Biallylamine.* — Impure allylamine obtained by either of the above-mentioned processes, is converted, by digestion with iodide of allyl, into a crystalline mixture of hydriodates, among which biallylamine doubtless occurs, though it has not yet been obtained free from the other bases.

*Triallylamine.*  $\text{C}^{18}\text{H}^{15}\text{N} = \text{N}(\text{C}^3\text{H}^5)^3$ . — Produced in the decomposition by heat of the hydrated oxide of tetrallylium. The distillate saturated with hydrochloric acid and mixed with bichloride of platinum yielded a pale yellow platinum-salt, containing 28.37 p. c. platinum. The formula  $\text{C}^{18}\text{H}^{15}\text{N}, \text{HCl}, \text{PtCl}^2$  requires 28.76 p. c. (Cahours & Hofmann.)

*Tetrallylium.*  $\text{C}^{24}\text{H}^{20}\text{N} = \text{N}, (\text{C}^3\text{H}^5)^4$ . — The iodide of this radical is the chief product of the action of ammonia on iodide of allyl, its formation taking place even when iodide of allyl is left in contact with aqueous ammonia. After a few days' contact, a considerable portion of

the iodide is generally dissolved and the residual layer is sometimes found crystallized. If this is not the case, the addition of potash-ley will separate an oily layer, which in a few minutes solidifies to a crystalline mass of iodide of tetrallylium. The compound may be purified by exposure to the air, whereby the adhering potash is converted into carbonate, and recrystallization from absolute alcohol. — The iodide gives by analysis 41.26 p. c. iodine, the formula  $C^4H^{20}NI$  requiring 41.66 p. c.

By treating the iodide with oxide of silver, the hydrated oxide is obtained, which is a strong alkaline base resembling the hydrated oxide of tetrethylum. Its solution in hydrochloric acid yields with bichloride of platinum a pale yellow salt, containing :

Cahours & Hofmann.					
24 C	.....	144.0	...	37.57	..... 37.40
20 H	.....	20.0	...	5.24	..... 5.19
N	.....	14.0	...	3.65	
3 Cl	.....	106.5	...	27.79	
Pt	.....	98.7	...	25.75	..... 25.88
<hr/>					
$C^4H^{20}NCl, PtCl^2$		383.2	...	100.00	

*Tetrallylarsonium.*  $C^4H^{20}As = As(C^4H^5)^4$ . — Produced, together with other compounds, by the action of iodide of allyl on arsenide of potassium. A number of liquid products are formed having an extremely offensive odour, and gradually rising in boiling point, so that their separation cannot well be effected, and at the same time a solid crystalline mass is obtained which is doubtless the iodide of tetrallyl-arsonium. (Cahours & Hofmann.)

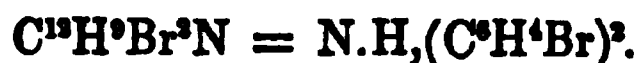
*Mercurallyl.*  $C^6H^5Hg^2$ . — When iodide of allyl is agitated with mercury, a yellow crystalline mass is formed from which the iodide of mercurallyl is easily extracted by hot alcohol or ether. The alcoholic solution deposits it on cooling, in silvery scales which turn yellow when exposed to light, especially on drying. It is sparingly soluble in cold alcohol, and nearly insoluble in water. At  $100^\circ$  it sublimes in white shining rhombic tables. At  $135^\circ$  it melts, and on cooling solidifies to a yellow crystalline mass. If more quickly and strongly heated, it decomposes for the most part, leaving a carbonaceous residue and giving off a yellow sublimate.

Iodide.				Zinin.	
6 C	.....	36	...	9.78	..... 9.59
5 H	.....	5	...	1.35	..... 1.38
I	.....	127	...	34.51	..... 34.49
2 Hg	.....	200	...	54.36	
<hr/>					
$C^6H^5HgI^2$ .....		368	...	100.00	

The alcoholic solution of iodide of mercurallyl is decomposed by nitrate of silver, the whole of the iodine being separated as iodide of silver. Oxide of silver also forms iodide of silver, and a strongly alkaline solution, which on evaporation yields a syrupy, strongly alkaline mass, soluble in water and forming salts with acids. When heated it smells like angelica and garlic. It is doubtless the hydrated oxide of mercurallyl. (Zinin, *Ann. Pharm.* 96, 363).



## Bibromallylamine.



MAXWELL & SIMPSON. *Ann. Pharm.* 109, 362; *Phil. Mag.* (4) 16, 257.

*Formation.* By the action of ammonia on terbromide of allyl:



*Preparation.* 1 vol. terbromide of allyl and 6 vol. of a solution of ammonia in dilute alcohol are heated together for 10 or 12 hours to 100° in sealed tubes. — Bromide of ammonium then separates; and on opening the tube and mixing the filtered liquid with a large quantity of water, bibromallylamine separates in the form of an oil. To purify this product, it is washed with water and dissolved in hydrochloric acid; the filtered solution is evaporated to dryness at 100°; the residue is dissolved in water; the liquid, separated by filtration from a small quantity of oil, is again evaporated to dryness; and the residue is washed with ether, in which the hydrochlorate is nearly insoluble, and dried in vacuo over sulphuric acid.

From the hydrochlorate thus obtained, the base is separated by dilute potash or ammonia, then washed with water and dried in vacuo over sulphuric acid. It is a heavy oily liquid having a peculiar sweet and aromatic taste: it fumes in the neighbourhood of strong hydrochloric acid, and exhibits an alkaline reaction with litmus paper.

				Simpson.
12 C .....	72	...	28.25	..... 28.93 to 29.22
9 H .....	9	...	3.53	..... 3.34 „ 3.86
2 Br .....	160	...	62.73	
N .....	14	...	5.49	
<hr/>				
$\text{C}^1\text{H}^3\text{Br}^2\text{N}$ ....	255	...	100.00	

Bibromallylamine cannot be distilled without decomposition. — Heated in a sealed tube with iodide of ethyl, it yields *hydriodate of ethyl-bibromallylamine*  $\text{N}(\text{C}^3\text{H}^5)(\text{C}^6\text{H}^4\text{Br})^2, \text{HI}$ .

Bibromallylamine dissolves very sparingly in water, but easily in alcohol, and in sulphuric, hydrochloric, nitric or acetic acid. It is however but a weak base, incapable of decomposing copper or silver salts, and exhibiting but little tendency to form crystallizable salts.

*Sulphate of Bibromallylamine* is obtained by dissolving the base in dilute sulphuric acid, removing the excess of sulphuric acid with carbonate of baryta, and evaporating the filtered solution. It is a gummy mass which shows no tendency to crystallize.

*Hydrochlorate of Bibromallylamine*, prepared as above, is a neutral slightly yellowish salt, which tastes like the base itself. It dissolves readily in water and in alcohol, sparingly in ether. Heated to 100° for some time, it acquires a dark colour, as if from incipient decomposition, but a much higher temperature is required to decompose it completely.



It sublimes partially at 160°. Nitrate of silver, added to the aqueous solution of this salt, throws down the chlorine but not the bromine.

						Simpson.		
12 C .....	72	....	24.69	.....	24.40	....	....	23.80
10 H .....	10	....	3.44	.....	3.64	....	....	3.76
N .....	14	....	4.80	.....	4.77	....	....	4.98
Cl .....	36.5	....	12.19	.....	....	12.65		
2 Br .....	160	....	54.88	.....	....	52.80		
<hr/>								
$C^{12}H^9Br^2N, HCl$ .... 292.5 .... 100.00								

An alcoholic solution of bibromallylamine, mixed with an alcoholic solution of *mercuric chloride*, forms a copious white precipitate.

*Chloroplatinate of Bibromallylamine.*  $C^{12}H^9Br^2N, HCl, PtCl^3$ . — On mixing the cold concentrated solutions of hydrochlorate of bibromallylamine and bichloride of platinum, an orange-yellow precipitate is formed, nearly insoluble in absolute alcohol. Dried at 100°, it gave by analysis, 15.78 p. c. carbon, 2.34 hydrogen, and 21.05 to 21.35 platinum, the formula requiring 15.61 C, 2.17 H, and 21.40 Pt. (Simpson).

**ETHYL-BIBROMALLYLAMINE.**  $C^{16}H^{13}NBr^2 = N, C^4H^5, (C^4H^4Br)^2$ . — The hydriodate of this base is obtained by heating bibromallylamine with excess of iodide of ethyl in a sealed tube, at the temperature of the water-bath. The hydriodate then separates as a heavy oil containing a few crystals; and on distilling off the excess of iodide of ethyl, dissolving the residual salt in warm water, and mixing the solution with potash, ethyl-bibromallylamine separates as a heavy oil, having an extremely bitter and pungent taste and an odour of nutmeg. It is insoluble in water, soluble in acids. It has an alkaline reaction, and is a stronger base than bibromallylamine, being capable of precipitating cupric oxide from the solutions of its salts. (Simpson.)

						Simpson.		
16 C .....	96	....	33.92	.....	34.21			
13 H .....	13	....	4.59	.....	4.87			
2 Br .....	160	....	56.53					
N .....	14	....	4.96					
<hr/>								
$C^{16}H^{13}Br^2N$ .... 283 .... 100.00								

Page 365.

### Acrolein.

GEUTHER & CARTMELL. *Ann. Pharm.* 112, 1; abstr. *Proc. Roy. Soc.* 10, 108.

*Action of Water.* Acrolein mixed with two or three times its volume of water, and heated to 100° for about a week, is gradually decomposed, yielding acrylic acid, and a resin agreeing nearly in composition with

Redtenbacher's *disacryl resin* (ix, 369): It gave by analysis 60.63, and 66.6 p. c. C; 7.6 and 7.4 H. Redtenbacher found 66.6 C, and 7.4 H. It differs, however, from Redtenbacher's compound in melting at a lower temperature, viz., 60°, and solidifying at 550°. It moreover gives off acrolein when heated, and reduces an ammoniacal solution of silver.

*Hydrochlorate of Acrolein.*  $C^6H^4O^2, HCl$ . — Produced by passing dry hydrochloric acid gas into anhydrous acrolein, in a vessel surrounded by cold water. The viscid product washed with water and dried over oil of vitriol, in vacuo, yields hydrochlorate of acrolein as a mass of white velvety crystals, which melt at 32° C. into a thick oil having the odour of rancid fat. It is insoluble in water, but readily soluble in alcohol or ether, on the evaporation of which it remains as a thick oil.

Geuther & Cartmell.					
6 C	.....	36.0	...	38.92	..... 39.32
5 H	.....	5.0	...	5.41	..... 5.78
Cl	.....	35.5	...	38.37	..... 35.88
2 O	.....	16.0	...	17.30	
<hr/>					
$C^6H^4O^2, HCl$		92.5	...	100.00	

The deficiency of chlorine and excess of carbon probably arose from the presence of a resinous modification of acrolein, like disacryl-resin.

Hydrochlorate of acrolein is resolved by heat into acrolein and hydrochloric acid. It is not apparently altered by boiling with water, or by the action of dilute solutions of the alkalis. Heated with ammonia to 100° in a sealed tube, it yields chloride of ammonium and acrolein-ammonia. Strong hydrochloric acid decomposes it, setting the acrolein free; a similar action is exerted by dilute sulphuric or nitric acid,—Hydrochlorate of acrolein in alcoholic solution does not combine with bichloride of platinum, and very slowly reduces a boiling ammoniacal solution of nitrate of silver.

Gaseous *hydriodic* acid, passed into acrolein, exerts a violent action attended with a hissing noise, like that of red-hot iron plunged into water. The product is a resinous body, which is insoluble in alcohol, ether, acids, and alkalis, and gives off iodine when heated, or when digested with bisulphide of carbon.

**METACROLEIN.** — Hydrochlorate of acrolein, heated with hydrate of potash, gives off hydrogen, and yields an oily distillate, which solidifies in magnificent, colourless, needle-shaped crystals, consisting of metacrolein, a compound isomeric or more probably polymeric with acrolein. (Analysis: 63.9 p. c. C, and 7.4 H; by calculation, 64.29 C, and 7.14 H. The evolution of hydrogen in the formation of this compound is due to a secondary action, part of the acrolein being at the same time converted into acetate and formate of potash.) Metacrolein is lighter than water, has an aromatic odour and a cooling taste with burning after-taste. It melts at 50°, solidifies at about 45°, and volatilizes a little before melting, so that it may be distilled with vapour of water. By heat it is changed into common acrolein. It is not affected by dilute alkalis, but when heated with mineral acids, it is changed more or less into acrolein. In a stream of dry hydrochloric acid gas, it melts, and is converted into the hydrochlorate of acrolein above described. Hence it is probable that the compound so named, is really a *hydrochlorate of metacrolein*, perhaps  $C^{12}H^8O^4, 2HCl$ .

*Hydriodate of Metacrolein* is produced by passing dry hydriodic acid gas over metacrolein, as a heavy yellow liquid, which resembles the hydrochlorate in taste and appearance, and after washing in water, shews a tendency to crystallize at ordinary temperatures. When placed over oil of vitriol, it decomposes, turning brown and giving off iodine.

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Page 397.

### Bromide of Propylene. $C^3H^6Br^2$ .

According to Wurtz (*N. Ann. Chim. Phys.* 52, 84), the process given by Dusart (*Compt. rend.* 41, 495), for preparing this compound, viz., to distil a mixture of equivalent quantities of acetate and oxalate of lime, and pass the evolved gases into bromine, does not yield a good product. Better results are obtained by Reynold's method (*Chem. Soc. Qu. J.*, 3, 111), of decomposing amylic alcohol by heat. Wurtz passes the vapour of amylic alcohol through a porcelain tube, heated to a temperature between bright and dull redness; passes the resulting gases through aqueous potash (which retains undecomposed amyl-alcohol and liquid hydrocarbons); receives the propylene gas in large flasks standing over water; then introduces liquid bromine into the flasks, which is thereby almost immediately decolorized; and subjects the crude bromide of propylene thus obtained to fractional distillation. Between  $125^\circ$  and  $138^\circ$ , a mixture of bromide of ethylene and bromide of propylene passes over; between  $138^\circ$  and  $150^\circ$ , nearly pure bromide of propylene; the portion which distils between  $150^\circ$  and  $200^\circ$  contains also bromide of butylene; above  $200^\circ$ , the residue gives off vapours of hydrobromic acid.

Bromide of propylene, purified by repeated fractional rectification, is a colourless liquid, which smells like chloride of ethylene and boils between  $140^\circ$  and  $145^\circ$ , nearer to the former. A portion boiling between  $137^\circ$  and  $140^\circ$ , gave by analysis 16.66 p. c. carbon, and 2.87 hydrogen; another portion boiling between  $140^\circ$  and  $144^\circ$ , gave 18.15 C, and 3.04 H, the formula  $C^3H^6Br^2$  requiring 17.82 C, and 2.98 H.

Bromide of propylene heated with 2 At. acetate of silver, yields acetate of propylene,  $C^3H^6(C^4H^3O^3)^2O^4$ , from which *propylic glycol* may be obtained by distillation with potash. (Wurtz.)

*Bromide of Bromopropylene.*  $C^4H^5Br, Br^2$ . — a. Bromide of propylene is but very slowly attacked by bromine. To replace 1 At. hydrogen in it by bromine, it is necessary to pass vapour of bromine into a large flask in which bromide of propylene is kept in a state of ebullition, so that the two bodies may mix in the state of vapour, the bromine which passes off uncombined being condensed in a cooled receiver, and continually passed through the apparatus till the proper quantity of it has been absorbed. The product is then purified by fractional distillation.

Colourless liquid. of sp. gr. 2.392 at 23°. Boils at about 195°. Has a very irritating and persistent odour.

					Wurtz.
6 C	.....	36	...	12.81	..... 12.68
5 H	.....	5	...	1.78	..... 1.62
3 Br	.....	240	...	85.41	
<hr/>					
$C^6H^5Br, Br^2$	....	281	....	100.00	

This compound acts with tolerable facility on silver-salts. When it is distilled with acetate of silver, the principal product, appears to consist of an acetic ether of the glycol  $C^6H^5O^4$ , viz.  $\frac{C^6H^5}{(C^4H^3O^2)^2} \left\{ O^4 \right.$ , the compound  $C^6H^5Br, Br^2$ , first giving up an atom of hydrobromic acid, and being reduced to  $C^6H^5Br^2$ , and this compound acting upon acetate of silver in a similar manner to bromide of ethylene or bromide of propylene. — At the same however, a secondary reaction is observed, resulting in the formation of a small quantity of triacetin,  $C^6H^5, (C^4H^3O^2)^2, O^6$ .

$\beta$ . A compound isomeric, if not identical with the preceding; is obtained by treating bromopropylene or bromide of allyl,  $C^6H^5Br$  (ix, 398), with bromine. This compound absorbs bromine with avidity; and if it be placed in a vessel surrounded with a frigorific mixture, and bromine added by small portions (4 pts. bromine to 3 pts. bromide of allyl), the reaction, which is at first very violent, becomes moderated as the addition of the bromine is continued, and at length there is obtained a liquid, which, after being washed with alkaline and then with pure water, and dried over chloride of calcium, distils entirely between 190° and 200°, the greater part passing over at 195°.

The compound thus obtained is a colourless liquid, agreeing in composition (12.56 to 12.61 p. c. carbon, and 1.76 to 1.89 hydrogen), specific gravity and boiling point with the preceding; but its odour is less irritating, being more like that of chloroform, and it acts less quickly on silver-salts. When immersed in a freezing mixture, it remains perfectly liquid. (Wurtz.)

These two compounds,  $\alpha$  and  $\beta$ , are isomeric with *terbromide of allyl*,  $C^6H^5Br^2$  (p. 544), obtained by the action of bromine on the compound  $C^6H^5I$ ; but they differ from it in their reaction with silver-salts. Terbromide of allyl distilled with acetate of silver, yields triacetin  $(C^6H^5)'''(C^4H^3O^2)^2O^6$ ; but bromide of bromopropylene  $\beta$ , distilled with acetate of silver, does not yield a trace of liquid volatile above 200° (triacetin boils at 268°). Bromide of bromopropylene  $\alpha$  yields, as the principal product of its reaction with acetate of silver, not, as already observed, a triatomic acetate or glycerin-compound, but a biatomic acetate, or glycol compound. And bromide of bromopropylene  $\beta$ , appears to act entirely in the latter way, not yielding a trace of triacetin; in fact the liquid produced by the reaction distils wholly below 200°, whereas triacetin boils at 268°. (Wurtz.)

Both these compounds  $\alpha$  and  $\beta$  are likewise distinguished from *terbromide of allyl* by their behaviour with ammonia and with sodium (p. 543).

Page 400.

## Hydrate of Propylene or Propylic Glycol.

A. WURTZ. *N. Ann. Chim. Phys.* 55, 440.

*Formation.* Bromide of propylene heated with acetate of silver, yields biacetate of propylene; and this distilled with hydrate of potash yields propylic glycol, the reactions being exactly similar to those which take place in the formation of ethylic glycol (xii, 501).

*Preparation.* 1 At. bromide of propylene is heated for four days to 100° with 2At. acetate of silver and a quantity of crystallizable acetic acid sufficient to form a uniform pulp; ether is then added; the bromide of silver separated by filtration; and the biacetate of propylene is distilled off between 140° and 200°. — To obtain the propylic glycol, the biacetate is decomposed by a boiling concentrated solution of baryta, added by small portions till the liquid becomes distinctly alkaline. The excess of baryta is then removed by a stream of carbonic acid; the filtered solution containing the glycol and acetate of baryta is evaporated over the water-bath, till the acetate of baryta begins to separate (if the evaporation be carried further, some of the glycol will be lost); the liquid is mixed with twice its volume of strong alcohol; and the solution, after filtration, is evaporated over the water-bath, till all the alcohol is expelled, after which the propylic glycol is distilled off and purified by rectification. The acetate of propylene may also be decomposed by distilling it with pulverized hydrate of potash, added by small portions, (2 At. potash to 1 At. of the acetate); but this method is not so convenient as the former.

*Properties.* Colourless, viscid, odourless liquid, having a saccharin taste. Sp gr. 1·051 at 0°, and 1·038 at 23°. Boils at 188° or 189°, the bulb and stem of the thermometer being immersed in the vapour, and a platinum wire introduced into the liquid. Distils without alteration to the last drop. Vapour-density 2·596.

					Wurtz.		Vol.		Density.
6 C .....	48	...	47·36	.....	47·11	C-vapour	6	...	2·4960
8 H .....	8	...	10·52	.....	10·73	H-gas	8	...	8·5544
4 O .....	32	...	42·12	.....	42·16	O-gas	2	...	2·2186
<hr/>									
C <sup>6</sup> H <sup>8</sup> O <sup>4</sup> ...	88	...	100·00	.....	100·00	Vapour	2	...	5·2690
							1	...	2·6345

*Decompositions.* 1. Propylic glycol is rapidly oxidized by nitric acid of sp. gr. 1·308, with evolution of nitric oxide, nitrogen, and carbonic acid, and formation of oxalic acid, together with a small quantity of another acid richer in carbon (probably malonic acid, C<sup>6</sup>H<sup>4</sup>O<sup>8</sup>). — Nitric acid of sp. gr. 1·148 oxidizes it almost as rapidly, but the chief product of the action is glycolic acid. In both these reactions, the propylic glycol

gives up 2 At. carbon, which are given off as carbonic acid, and yields products similar to those derived from the 4-carbon glycol. — 2. A slower and more regular action is obtained by dropping an aqueous solution of propylic glycol on a mixture of spongy platinum and platinum black. In this case, the chief product of the action is lactic acid :



A small quantity of glycolic acid is likewise formed. — 3. Propylic glycol may also be oxidized by permanganate of potash, and in that case the chief product of the oxidation is acetic acid. — When propylic glycol is heated to about  $250^\circ$  with hydrate of potash, hydrogen is evolved and oxalate of potash is formed, together with a smaller quantity of another salt which appears to be lactate. — 4. Pentachloride of phosphorus acts violently on propylic glycol, even when cooled by a freezing mixture, producing hydrochloric acid, oxychloride of phosphorus, and chloride of propylene :



5. Chloride of zinc exerts a dehydrating action upon propylic glycol, producing propylic aldehyde ( $\text{C}^6\text{H}^8\text{O}^4 - 2\text{HO} = \text{C}^6\text{H}^6\text{O}^2$ ); other products are likewise formed resembling those obtained under similar circumstances from ethylic glycol. The propylic aldehyde formed in this reaction yielded by analysis 61.5 p. c. carbon and 10.6 hydrogen, the formula  $\text{C}^6\text{H}^6\text{O}^2$  requiring 62.1 C and 10.3 H; the excess of hydrogen probably arose from the presence of a little water. — 6. Propylic glycol dissolves *sodium*, with evolution of hydrogen.

*Combinations.* Propylic glycol dissolves in all proportions in *water* and in *alcohol*. It is insoluble in a small quantity of *ether*, but dissolves completely in 10 or 12 times its volume of that liquid.

*Biacetate of Propylene.*  $\text{C}^{14}\text{H}^{12}\text{O}^8 = \text{C}^6\text{H}^6, (\text{C}^4\text{H}^3\text{O}^2)^2, \text{O}^4$ . — *Propylglycol diacetique.* — (*Preparation.* p. 554.) — It is purified by repeated fractional distillation, that portion being collected which boils above  $180^\circ$ .

Colourless neutral liquid, emitting the odour of acetic acid, especially when warmed. Sp. gr. 1.109. Boils at  $186^\circ$ , under a pressure of 0.758 met.

					Wurtz.
14 C .....	84	...	52.5	.....	52.6
12 H .....	12	...	7.5	.....	7.6
8 O ... ..	64	...	40.0	.....	39.8
<hr/>					
$\text{C}^{14}\text{H}^{12}\text{O}^8$ ...	160	...	100.0	.....	100.0

The compound is easily saponified by potash or baryta. 0.438 grm. of the liquid heated in a sealed tube, yielded a liquid which, when freed from excess of baryta by carbonic acid and precipitated by sulphuric acid, gave 0.656 grm. sulphate of baryta, corresponding to 2.05, that is to say 2 At. acetic acid.

Biacetate of propylene is insoluble in a small quantity of water, but dissolves in about 10 times its volume of water, forming a solution which is neutral to the taste, but slightly acid to test paper. — It dissolves in all proportions in alcohol and in ether.

We may here describe the glycols of the butyl and amyl series.

### Hydrate of Butylene or Butylic Glycol.



WURTZ. *N. Ann. Chim. Phys.* 55, 452.

*Preparation.* Biacetate of butylene is obtained by heating bromide of butylene  $\text{C}^4\text{H}^8\text{Br}^2$  with acetate of silver, exhausting the product with ether, and submitting the solution to fractional distillation; and this product distilled with pulverized hydrate of potash added by small portions, yields butylic glycol, which may be purified by another distillation with the pulverized hydrate of potash, and subsequent rectification *per se*.—The decomposition of the biacetate might also be effected by baryta-water; but the use of that alkali is less advantageous, because a considerable quantity of the butylic glycol is lost during the evaporation of the mixture of acetate of baryta and butylic glycol over the water-bath.

*Properties.* Thick, colourless, inodorous liquid, having a sweet aromatic taste. Sp gr. 1.048 at 0°. Boils at 183° or 184°, the bulb and stem of the thermometer being surrounded by the vapour. Vapour-density 3.188.

					Wurtz.			Vol.	Density.
8 C .....	48	....	53.33	.....	53.13	C-vapour.....	8	....	3.3280
10 H .....	10	....	11.11	.....	11.32	H-gas .....	10	....	0.6930
4 O .....	32	....	35.56	.....	35.55	O-gas .....	2	....	2.2186
$\text{C}^4\text{H}^{10}\text{O}^4$ ....	90	....	100.00	.....	100.00	Vapour .....	2	....	6.2396
							1	....	3.1198

Nitric acid, even if dilute, strongly attacks butylic glycol, producing oxalic acid; but if the action be made to take place very slowly, as when the acid and the glycol are disposed in separate layers in a narrow cylinder, butylactic acid  $\text{C}^4\text{H}^8\text{O}^4$  is produced as well as oxalic acid. On evaporating the acid liquid, redissolving in water and neutralizing with chalk; then evaporating the filtrate, treating the residue with alcohol, and precipitating the alcoholic solution with chalk; again filtering and evaporating, treating the residue with water, and neutralizing the warm aqueous extract with hydrocarbonate of zinc—a salt was obtained which gave by analysis 34.4 p. c. carbon and 6.1 hydrogen, the formula of butylacetate of zinc  $\text{C}^4\text{H}^7\text{ZnO}^6$  requiring 36.4 p. c. C and 5.1 H.—Butylic glycol is decomposed by caustic potash and soda, though less easily than ethylic glycol, with evolution of hydrogen and formation of oxalic acid and other products.

Butylic glycol is soluble in all proportions in water, alcohol, and ether. Its solubility in ether distinguishes it from the ethylic and propylic glycols, which are but sparingly soluble in that liquid.

*Biacetate of Butylene.*  $\text{C}^4\text{H}^{14}\text{O}^8 = \text{C}^4\text{H}^8(\text{C}^4\text{H}^3\text{O}^3)^2, \text{O}^4$ .—*Butyl-glycol diacetique.*—Obtained by the action of bibromide of butylene on acetate of silver, and purified by subjecting to fractional distillation the portion of the volatile product which boils above 140°, collecting apart that which distils above 190°, rectifying it by acetate of silver, and again distilling.



Colourless oily liquid, odourless when cold, but smelling faintly of acetic acid when heated. Boils at about 200°.

					Wurtz.
16 C .....	128	...	55.17	.....	53.66 to 54.88
14 H .....	14	...	8.04	.....	8.09 „ 8.29
8 O .....	64	...	36.79		
<hr/>					
$C^8H^8(C^4H^3O^2)^2, O^4$	206	...	100.00		

Easily decomposed by alkalis into acetic acid and butylic glycol. Insoluble in water; soluble in alcohol and ether.

### Hydrate of Amylene or Amylic Glycol.



WURTZ. *N. Ann. Chim. Phys.* 55, 458.

Preparation similar to that of the preceding compounds. The bromide of amylene required for the purpose is obtained by adding bromine in successive small portions to rectified amylene contained in a long-necked flask surrounded by a freezing mixture. On rectifying the product, the greater part distils between 170° and 180°, but is at the same time partially decomposed, with evolution of hydrobromic acid. Hence it is better, when the product is to be used for the preparation of amylic glycol, to stop the distillation when the temperature rises to 160°, and treat the residue, without further purification, with acetate of silver mixed with glacial acetic acid. This reaction takes place easily at ordinary temperatures, giving rise to great evolution of heat. — The acetate of amylene thus obtained is decomposed by distillation with dry potash, as in the preparation of butylic glycol.

*Properties.* Colourless, very syrupy liquid, having a bitter taste with aromatic aftertaste. When cooled by a mixture of solid carbonic acid and ether, it solidifies into a hard transparent mass. It does not affect polarized light. Sp. gr. 0.987 at 0°. Boils at 177° and distils without alteration.

					Wurtz.
10 C .....	60	...	57.69	.....	57.77
12 H .....	12	...	11.53	.....	11.67
4 O .....	32	...	30.78	.....	30.56
<hr/>					
$C^{10}H^{12}O^4$ .....	104	...	100.00	.....	100.00

Amylic glycol when pure is soluble in water in all proportions. If not carefully prepared, it leaves when dissolved in water a few oily drops of a compound which raises its boiling point.



The aqueous solution turns acid when exposed to the air in contact with platinum-black, yielding chiefly carbonic acid, with only a small quantity of a fixed acid, apparently butylactic acid. It is remarkable that the slow oxidation of the glycols under the influence of platinum-black, is less regular as the molecule is more complicated. Ethylic glycol thus treated is easily converted into glycolic acid; the conversion of propylic glycol into lactic acid is more difficult, taking place only under peculiar conditions; and amylic glycol yields but a very small quantity of a fixed acid belonging to the lactic acid series. — Amylic glycol gently heated with nitric acid (14 grm. of the glycol to a mixture of 30 grm. fuming nitric acid and 42 grm. water) is rapidly oxidized, yielding as the chief product butylactic acid  $C^8H^{10}O^6$ . The baryta-salt of the acid thus obtained yielded 28.33 p. c. C, 3.86 p. c. H and 40.00 Ba, the formula  $C^8H^7BaO^6$  requiring 27.98 C, 4.08 H and 39.94 Ba; the zinc-salt gave by analysis 34.68 and 35.45 p. c. C, and 5.10 and 5.52 H, the formula  $C^8H^7ZnO^6$  requiring 35.42 C and 5.16 H.

*Biacetate of Amylene.*  $C^{18}H^{16}O^8 = C^{10}H^{10}(C^4H^3O^2)^2, O^4$ . — Colourless neutral liquid, insoluble in water, boiling above  $200^\circ$ , and easily decomposed by alkalis into acetic acid and amylic glycol.

					Wurtz.
18 C	.....	128	....	57.44	..... 56.88
16 H	.....	16	....	8.51	..... 9.10
8 O	.....	64	....	34.05	..... 34.02
<hr/>					
$C^{18}H^{16}O^8$	.....	208	....	100.00	..... 100.00

Page 402.

**PROPIONIC ACID.** — This acid is found among the products of the distillation of Irish peat (Sullivan, *Atlantis*, 1, 185), and in small quantity among those of the fermentation of diabetic urine. (Klänger, *Ann. Pharm.* 106, 18). It likewise occurs in certain mineral waters (Scherer, *Ann. Pharm.* 99, 257; Fresenius, *J. pr. Chem.* 70, 1); in guano (Lucius, *Ann. Pharm.* 103, 105); in putrid yeast (Hesse, *J. pr. Chem.* 71, 1); and in certain fungi (Bornträger, *N. Jahrb. Pharm.* 8, 222).

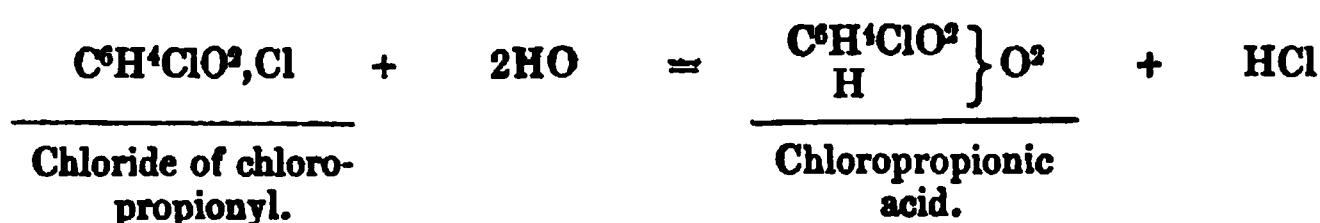
*Artificial Formation.* 1. Sodium-ethyl exposed to the action of dry carbonic acid gas is converted into propionate of soda (p. 491):



The acid liberated from the soda-salt by distillation with sulphuric acid, yielded a silver-salt which gave by analysis 19.29 p. c. C, 2.71 H and 59.65 Ag, the formula  $C^6H^5AgO^4$  requiring 19.89 C, 2.76 H and 59.67 Ag. (Wanklyn, *Chem. Soc. Qu. J.* 11, 103.)

2. *From Lactic Acid.* — Wurtz (*Ann. Pharm.* 107, 192) obtained by the action of pentachloride of phosphorus on lactic acid ( $C^3H^5O^3$ ), an

organic chloride, which he regarded as *chloride of lactyl*,  $C^6H^4O^2,Cl^2$ . It gave by analysis 27·6, 27·5 and 29·3 p. c. C, 3·3 and 3·1 H and 50·4 Cl, the formula requiring 28·3 C, 3·1 H and 55·9 Cl. He further states that it yields lactic acid when treated with water, and *chlorolactic ether*,  $C^6H^4ClO^4,C^4H^6$ , with alcohol. According to Ulrich, on the other hand (*Chem. Soc. Qu. J.* 12, 23), the formation of lactic acid from this chloride by the action of water, takes place only when an alkaline base is present; when the decomposition is produced by the action of water alone, the product is not lactic, but *chloropropionic acid*  $C^6H^4ClO^4$ ; and this compound, when subjected to the action of nascent hydrogen, is converted into lactic acid. Hence Ulrich regards the chloride in question as *chloride of chloropropionyl*.



*Chloropropionic Acid.* — To prepare this compound, the colourless fuming mixture of chloride of chloropropionyl obtained by heating dry lactate of lime with pentachloride of phosphorous, is added by small portions to a large quantity of water; and the acid liquid containing chloropropionic acid together with considerable quantities of phosphoric and hydrochloric acid, is evaporated to half its bulk. The distillate contains hydrochloric and chloropropionic acids (no lactic is found in the residue); and on neutralizing it in the cold with recently precipitated carbonate of silver, and evaporating the filtered solution in vacuo, chloropropionate of silver is obtained in beautiful colourless square prisms, containing :

				Ulrich.
6 C .....	36·0	...	16·7	16·5
4 H .....	4·0	...	1·9	1·9
Cl .....	35·5	...	16·5	
Ag .....	108·0	...	50·1	50·2
4 O .....	32·0	...	14·8	
<hr/>				
$C^6H^4ClAgO^4$ .....	215·5	...	100·0	

This salt when heated gives off a small portion of the chloropropionic acid undecomposed, so that the residue obtained on ignition contains a little metallic silver mixed with the chloride. It is much more soluble in water than propionate of silver, and is but little blackened by light. On boiling the aqueous solution or evaporating it over the water-bath, chloride of silver is deposited and lactic acid is doubtless formed.

Chloropropionic acid is reduced by nascent hydrogen to propionic acid. — When the crude chloride of chloropropionyl, still containing oxychloride of phosphorus, is made to flow gradually into water contained in a vessel well cooled from without, and having at bottom a large quantity of finely granulated zinc, a large quantity of hydrogen is evolved by the mutual action of the zinc, the water, and the phosphoric and hydrochloric acids; and by distilling this liquid, after the odour of the chloride of chloropropionyl and the oxide of phosphorus has disappeared, a distillate is obtained, containing considerable quantities of propionic acid. The

silver-salt prepared from this acid yielded by analysis 19·6 p. c. C, 2·8 H and 59·8 Hg, the formula  $C^6H^5AgO^4$  requiring 19·6 C, 2·8 H and 59·6 Hg. This method of preparing propionic acid is very productive and yields a pure product. (Ulrich.)

*Chloropropionate of Ethyl*,  $C^6H^4ClO^4, C^4H^6$ , (Wurtz's chlorolactate) decomposed by zinc and dilute sulphuric acid, yielded only traces of propionate of ethyl, but considerable quantities of propionic acid, the propionic ether being resolved at the moment of its formation into propionic acid and alcohol. (Ulrich.)

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Page 441.

*Butyracetic acid*. This acid, which is isomeric with propionic acid, may be prepared by the direct union of its constituents. When dilute sulphuric acid is gradually added to an aqueous solution of an acetate and a butyrate, in equivalent proportions, the two acids combine as they are liberated. The product, which is butyracetic acid, yields, when neutralized with *baryta*, a salt which has the composition of propionate of baryta,  $C^6H^6BaO^4 + Aq$ , but crystallizes in rhomboidal prisms. — The *lime-salt* has likewise the composition of propionate of lime, but crystallizes in efflorescent regular octohedrons, whereas the propionate crystallizes in long prisms, united in tufts. — The acid easily resolves itself into its constituent acids, as for example, when its baryta-salt is decomposed by sulphate of copper. (Nickles, *N. J. Pharm.* 33, 351).

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Page 417.

### Malonic Acid. $C^6H^4O^8$ .

DESSAIGNES. *Compt. rend.* 47, 76; *Ann. Pharm.* 107, 251.

*Formation*. By the oxidation of malic acid.

*Preparation*. A lump of bichromate of potash is introduced into a somewhat dilute solution of malic acid, and replaced by another as soon as its action is exhausted, the liquid being kept cool. Carbonic acid is then evolved, the mixture smells of malic acid, and becomes first green, then blue, and finally brown, when the weight of bichromate added is nearly equal to that of the malic acid. The dilute and moderately heated solution is now to be mixed with excess of milk of lime to preci-

pitato the chromic oxide ; the greenish filtrate is mixed with acetate of lead ; and the precipitate (containing a large quantity of chromate of lead) is mixed with just sufficient nitric acid to dissolve the malonate of lead. The filtrate, three-fourths saturated with ammonia, deposits the lead-salt in white flocks, which after washing, may be decomposed by sulphuretted hydrogen. The filtered liquid concentrated at a gentle heat, yields crystalline laminæ of malonic acid, together with a syrup consisting of malic acid containing chromic oxide, from which the crystals may be purified by draining and recrystallization. Bimalate of lime is also slowly oxidized by bichromate of potash ; the product however, is not malonic but oxalic acid. Neither is malonic acid produced by the action of peroxide of lead on free malic acid.

*Properties.* Large rhombohedral crystals, having a laminated structure and acid taste. Melts at  $140^{\circ}$ .

				Dessaigues.
6 C .....	36	...	34.61	..... 34.40
4 H .....	4	...	3.85	..... 3.91
8 O .....	64	...	61.54	..... 61.69
<hr/>				
$C^6H^4O^8$ .....	104	...	100.00	..... 100.00

Forms the second term of the series of bibasic acids  $C^nH^{n-2}O^8$ , being intermediate between oxalic acid  $C^2H^2O^8$  and succinic acid  $C^4H^6O^8$ .

Malonic acid gives off carbonic acid at  $150^{\circ}$ , and distils without residue, being however, partly resolved into a mixture of acetic and unaltered malonic acid, which may be easily separated by a second distillation.



Heated with oil of vitriol, it decomposes and becomes coloured.

Malonic acid dissolves readily in water and in alcohol. The concentrated aqueous solution forms with acetate of lead, a pulverulent precipitate ; with mercurous nitrate, a precipitate which blackens when heated ; it reduces chloride of gold when heated therewith. The concentrated solution gives no precipitate with acetate of potash, but precipitates the acetates of lime and baryta, and nitrate of silver ; these precipitates dissolve on addition of water. — Neutral malonate of ammonia is precipitated by the salts of calcium, barium, and mercury, and almost completely decolorizes sesquichloride of iron ; ammonia added to the mixture throws down ferric oxide.

The neutral malonates of *potash* and *ammonia* are deliquescent, but may be crystallized in a dry atmosphere ; the acid malonates of these bases crystallize readily in well defined crystals. Acid malonate of ammonia is resolved by dry distillation into acetate of ammonia, carbonic acid, and bicarbonate of ammonia.

*Malonate of baryta* forms silky tufts ; the *lime-salt* forms small transparent needles.

*Malonate of Silver.*  $C^6H^3Ag^2O^8$ , is a crystalline powder, which does not blacken at the boiling heat.

Dessaigues.					
6 C	.....	86	....	11.32	
2 H	.....	2	....	0.63	
2 Ag	.....	216	....	67.92	..... 67.97 .... 67.65
8 O	.....	64	....	20.13	
<hr/>					
$C^6H^3Ag^2O^8$	.....	318	....	100.00	

Page 459.

### Cyanurate of Ethyl.

A. HABICH & H. LIMPRICHT. *Ann. Pharm.* 109, 101; abstr, *Ann. Pharm.* 105, 395; *J. pr. Chem.* 74, 74.

For the preparation of this compound, the authors adopt the method originally given by Wurtz, viz., the distillation of a mixture of cyanurate and sulphovinate of potash. [Wurtz, (*Rep. Chim.* 1, 216), now recommends the cyanate of potash, as more convenient than the cynurate]. The distillate, which is only partly crystalline, contains, in addition to cyanuric ether, carbonate of ammonia, ethylamine, cyanide of ethyl, and other products. The solution of this distillate in alcohol, after being boiled till nearly clear, deposits, first a flocculent precipitate, and then crystals of cyanuric ether, which may be purified by recrystallization from dilute alcohol. — Cyanuric ether is also produced by heating bibasic or tribasic cyanurate of silver to  $120^\circ$  with iodide of ethyl.

*Properties.* Cyanuric ether forms crystals belonging to the rhombic system.  $\infty P$ .  $\infty \check{P} \infty$ .  $\check{P} \infty$ . Ratio of the axes =  $0.4877 : 1 : 0.9407$ .  $\infty P : \infty P$  in the brachydiagonal section = 128;  $\check{P} \infty : \check{P} \infty$  in the same =  $93^\circ 30'$ . (Rammelsberg, *Jahresber d. Chem.* 1857, 273.) It melts at  $95^\circ$ , and boils at  $253^\circ$  (as originally determined by Wurtz); volatilizes readily with vapour of water, and dissolves readily and without decomposition in acids, even in concentrated nitric acid.

Wurtz.						Habich & Limpricht.			
18 C	.....	108	....	50.7	.....	50.7	....	50.6	.... 60
15 H	.....	15	....	7.0	....	7.0	....	8.1	.... 71
3 N	.....	42	....	19.7	.....	20.0	.....	19.7	
6 O	.....	48	....	22.6	.....	22.3			
<hr/>									
$C_7^3(C^4H^5)^3O^8$	.....	213	....	100.0	.....	100.0			

Cyanuric ether is not decomposed by distillation with pentachloride of phosphorus. When boiled with alkalis, it is not immediately resolved

into carbonic acid and ethylamine (according to the equation:  $C^{18}H^{16}N^3O^6 + 6HO = 3C^4H^7N + 6CO^2$ ), but intermediate products are formed, which are most easily isolated when baryta is the alkali used. On boiling the ether with baryta-water, carbonate of baryta is precipitated, and the solution, freed from excess of baryta by carbonic acid, yields on evaporation, a liquid having the composition  $C^{16}H^{17}N^3O$ :



This liquid dissolves sparingly in water, readily in alcohol and ether, and is resolved by distillation, between  $170^\circ$  and  $200^\circ$ , into cyanate of ethyl and biethyl-urea:



*Chlorocyanuric ether.*  $C^{18}H^{11}Cl^4N^3O^6$ . — Produced by heating cyanuric ether to  $150^\circ$  in dry chlorine gas, as long as hydrochloric acid continues to be evolved. It may be purified by repeated solution in absolute alcohol and precipitation by water, and after drying over oil of vitriol, forms a hard transparent mass which is decomposed by heat.

					Habich & Limpricht.		
18 C	.....	108	...	30.8	.....	30.6	... 31.9
11 H	.....	11	...	3.1	.....	3.5	... 3.3
4 Cl	.....	142	...	40.4	.....	39.5	... 40.0
3 N	.....	42	...	11.9			
6 O	.....	48	...	13.8			
<hr/>							
$C^{18}H^{11}Cl^4N^3O^6$	.....	351	...	100.0			

It is decomposed at ordinary temperatures by alcoholic potash, yielding chloride of potassium, carbonate of potash, and a substance resembling chlorocyanuric ether, and having the composition  $C^{16}H^{11}Cl^2N^3O^4$ :



The substance thus produced yielded by analysis 38.9 p. c. C, 5.4 H, and 28.9 Cl, agreeing approximately with the formula  $C^{16}H^{11}Cl^2N^3O^4$ , which requires 38.1 C, 4.4 H, and 28.2 Cl. The quantities of carbonate and chloride of potassium obtained corresponded to between 13 and 14 p. c.  $CO^2$ , and 20 and 21 Cl, the above equation requiring 12.3 p. c.  $CO^2$  and 20.3 Cl.

*Hydrochlorate of Cyanic ether.*  $C^3H^5NO^3, HCl$ . — Produced: 1. By the action of hydrochloric acid gas on cyanuric ether. — 2. By the action of hydrochloric acid gas on biethylurea, hydrochlorate of ethylamine being formed at the same time:



It is also produced by the action of chlorine gas on biethylurea.

Colourless liquid, which boils at 95°, and has a penetrating, tear-exciting odour.

				Habich & Limpricht.	
6 C	.....	36.0	....	33.4	..... 33.6
6 H	.....	6.0	....	5.6	..... 5.6
N	.....	14.0	....	13.0	..... 10.8
Cl	.....	35.5	....	33.0	..... 33.4
2 O	.....	16.0	....	15.0	..... 16.6
<hr/>					
C <sup>6</sup> H <sup>5</sup> NO <sup>2</sup> ,HCl	.....	107.5	....	100.0	..... 100.0

Hydrochlorate of cyanic ether is instantly decomposed by water, yielding carbonic acid and hydrochlorate of ethylamine :



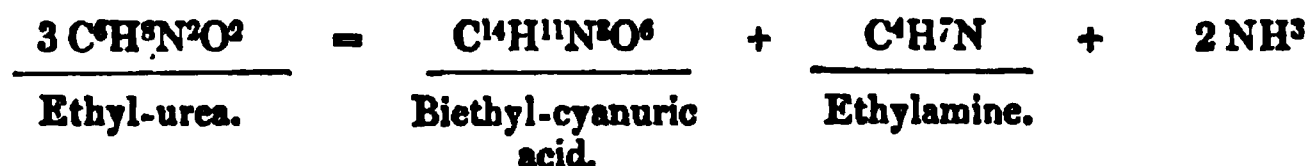
### Biethylcyanuric Acid.



WURTZ. *N. Ann. Chim. Phys.* 50, 120.

HABICH & LIMPRICHT. *Ann. Pharm.* 109, 112.

Produced : 1. In the decomposition of ethyl-urea by heat. (Wurtz) :



2. Together with cyanuric ether, in the distillation of a mixture of cyanurate and sulphovinate of potash (Habich and Limpricht). The mother-liquor (p. 562), from which the cyanuric ether has crystallized, yields, after evaporation of the alcohol, a brown viscid residue ; and on boiling this residue with water, as long as volatile bases continue to escape, then precipitating the excess of baryta by carbonic acid, and evaporating the filtrate, the oily body C<sup>16</sup>H<sup>17</sup>N<sup>3</sup>O<sup>6</sup> (p. 563) separates out first, and then after some time, crystalline crusts of biethylcyanurate of baryta ; and by decomposing the hot aqueous solution of this salt with sulphuric acid, biethylcyanuric acid is obtained in hard transparent crystals belonging to the hexagonal system. It melts at 173°, and volatilizes undecomposed at a higher temperature.

				Habich & Limpricht.	
14 C	.....	84	....	45.4	..... 45.1
11 H	.....	11	....	5.9	..... 6.2
3 N	.....	42	....	22.7	
6 O	.....	48	....	26.0	
<hr/>					
C <sup>6</sup> N <sup>3</sup> O <sup>6</sup> , (C <sup>4</sup> H <sup>5</sup> ) <sup>2</sup> H	.....	185	....	100.0	

The acid heated with baryta-water in a sealed tube to a temperature above  $100^{\circ}$ , yields ethylamine and carbonate of baryta, but not the oily body  $C^{16}H^{17}N^3O^6$ . Fused with hydrate of potash, it gives off ethylamine, and probably also ammonia.

Biethylecyanuric acid dissolves readily in ether, alcohol, and hot water, sparingly in cold water. — It dissolves easily in dilute ammonia, potash or baryta-water, but crystallizes out unaltered when the liquid is evaporated. It does not absorb gaseous ammonia. The ammoniacal solution forms with *cupric* acetate a rose-coloured precipitate, amorphous at first, but soon becoming crystalline, and forming with ammonia a blue solution, which when evaporated deposits long blue needles of variable composition. — The ammoniacal solution of biethylecyanuric acid forms a precipitate with *mercurous* nitrate in the cold; if, however, the solutions are hot, small concentrically grouped needles are deposited on cooling. — Similarly with acetate of *lead*; a hot solution deposits the lead-salt in nodular crystalline masses. This salt, distilled with sulphovinate of potash, yields cyanuric ether.

*Silver-salt.* The ammoniacal solution of the acid mixed with nitrate of silver, deposits this salt on cooling, in needles which may be purified by recrystallization from hot water. They are white, but gradually become darker by exposure to light. When heated, they melt, and yield a sublimate of biethylecyanuric acid.

				Habich & Limpricht.	
14 C	.....	84	....	28.7	..... 28.4
10 H	.....	10	....	3.4	..... 3.6
Ag	.....	108	....	36.9	..... 36.5
3 N	.....	42	....	14.4	..... 13.5
6 O	.....	48	....	16.6	..... 18.0
<hr/>				<hr/>	
$C^8N^3O^6(C^4H^5)_2Ag$	....	292	....	100.0	..... 100.0

Page 466.

*Liquid Chloride of Cyanogen*,  $Cy^2Cl^2$ , is produced in considerable quantity, together with the gaseous chloride, when a solution of cyanide of mercury (prepared by boiling prussian blue with mercuric oxide and water), is saturated with chlorine at a low temperature (—  $7^{\circ}$  and under), and may be condensed in a series of U-tubes attached to the apparatus. The liquid thus obtained boils at  $15^{\circ}$ , and agrees in its other properties with Wurtz's compound. Its solution in anhydrous ether treated with ammonia, yields chloride of ammonium and *cyanamide*,  $NCyH^2$ . (viii, 145):



The cyanamide obtained by evaporating the filtered solution melts at  $40^{\circ}$ , is converted at  $150^{\circ}$  into solid melamine, and yields nitrate of urea when its ethereal solution is heated with a small quantity of nitric acid. (W. Henke, *Ann. Pharm.* 106, 286.)



### Cyanetholine. $C^6H^5NO^3$ ,

CLOEZ. *Compt. rend.* 44, 482; *Ann. Pharm.* 102, 354.

Produced by the action of chloride of cyanogen on ethylate of sodium:



Gaseous chloride of cyanogen slowly passed into a solution of ethylate of sodium in absolute alcohol, is absorbed, with considerable rise of temperature, and chloride of sodium separates out; and on distilling the liquid separated therefrom, alcohol and excess of chloride of cyanogen pass over, and there remains a syrupy liquid which may be freed from chloride of sodium by washing. This liquid is cyanetholine, a compound isomeric with cyanide of ethyl. It is insoluble in water, but dissolves in all proportions in alcohol and ether. Sp. gr. 1.1271 at 15°. Its taste is somewhat bitter, and persistently disagreeable; it has a faint odour, somewhat like that of sweet oil of wine. When heated, it gives off a liquid, and leaves a black carbonaceous residue. Heated with strong potash-ley, it is decomposed and gives off ammonia (no ethylamine is formed).

Cyanetholine dissolves in most acids, forming crystallizable salts. The *sulphate* crystallizes in small prisms when its aqueous solution is evaporated over oil of vitriol. — The *hydrochlorate* forms a yellow double salt with bichloride of platinum; The *nitrate* forms with nitrate of silver, a double salt which separates in large crystals. — On passing nitric oxide gas into the solution of the nitrate, that salt is decomposed, with evolution of nitrogen and formation of a crystallizable substance not yet examined.

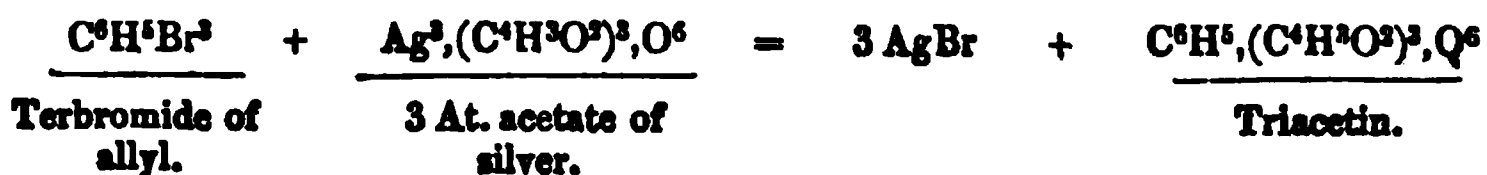
The sodium-compounds of other alcohols treated in like manner with chloride of cyanogen, may be expected to yield a series of homologous bases running parallel with that which contains glycol, alanine and leucine. (Cloez.)

Page 486.

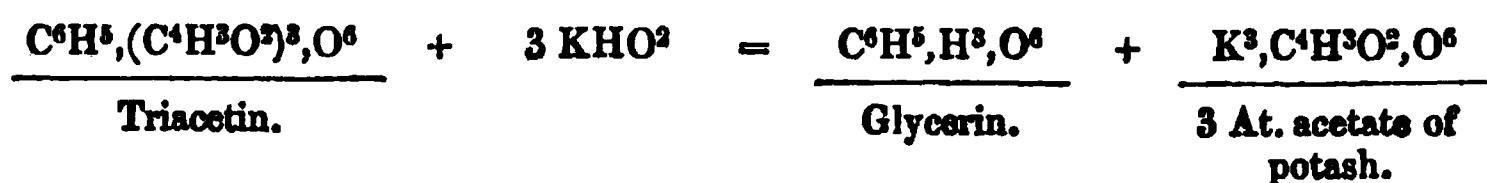
### Glycerin.

**Formation.** Pasteur has shewn that glycerin is always produced in the alcoholic fermentation of sugar, to the amount of about 3 per cent. of the sugar decomposed; and that it occurs in all fermented liquors, especially in wine (*Compt. rend.* 46, 857; 47, 224; *Ann. Pharm.* 106, 338).

**Artificial formation of Glycerin.** — Terbromide of allyl (p. 542), heated with acetate of silver, yields triacetin (ix, 497):



and triacetin distilled with caustic alkalis yields glycerin :



115 grammes of terbromide of allyl, dissolved in 5 or 6 times their bulk of crystallizable acetic acid, are mixed with 205 grms. of acetate of silver; and the mixture is kept for a week at a temperature of 120° to 125°. The liquid is then separated by filtration from the bromide of silver produced by the decomposition; the latter is washed with ether; the filtrate, together with the washings, is heated in a distillatory apparatus to 140°; the residue is neutralized with lime and digested with ether; and the yellowish oil which remains after evaporating the ethereal solution, is distilled. A distillate is then obtained, nearly the whole of which passes over above 250°, the greater portion at 268°; it has the properties and composition of triacetin. (It gave by analysis 49·12 p. c. carbon, and 6·60 hydrogen; the formula  $\text{C}^{18}\text{H}^{14}\text{O}^{12}$ , requires 49·54 carbon, and 6·42 hydrogen.)

To prepare glycerin from the triacetin thus produced, the latter is decomposed by baryta-water; the liquid is freed from excess of baryta by means of carbonic acid, and evaporated; the residue is treated with anhydrous alcohol containing a little ether; and the solution thus produced is evaporated. Glycerin then remains in the form of a syrupy liquid, very soluble in water and alcohol, insoluble in ether. — After being distilled in vacuo, it exhibited the sweet taste of ordinary glycerin, and gave by analysis 39·77 p. c. carbon, and 8·95 hydrogen, the formula  $\text{C}^6\text{H}^8\text{O}^6$ , requiring 39·13 and 8·69. Treated with biniodide of phosphorus, it yielded iodide of allyl. (Wurtz, *N. Ann. Chim. Phys.* 51, 97.)

*Bromide of bromopropylene*,  $\text{C}^6\text{H}^5\text{Br}, \text{Br}^2$  (p. 553), which is isomeric with terbromide of allyl, yields but a small quantity of triacetin when treated with acetate of silver; and the other modification of it obtained by treating bromide of allyl with bromine, yields none at all.

[For the action of nitric acid on glycerin see page 569.]

*Conversion of Glycerin into Sugar.* — A moderately concentrated aqueous solution of glycerin, left for some weeks in contact with certain animal membranes, especially the membranes of the testicle or of the pancreas, is found to contain a substance exhibiting the properties of grape-sugar. The best mode of effecting the transformation is to introduce the finely chopped membrane of the testicle, either of man or of other animals, to a solution of 1 pt. of glycerine in 10 pts. water, the quantity of membrane being about  $\frac{1}{50}$  that of the glycerine, and leave the liquid in an open flask exposed to diffused daylight, at a temperature of 10° to 20°. Under these circumstances, the animal membrane does not usually putrefy (if it does, the experiment fails), but after an interval, varying from one into twelve weeks, the liquid is found to contain a saccharine substance, which reduces oxide of copper in alkaline solution, and immediately ferments when mixed with beer yeast. The quantity of sugar thus produced is very variable. (Berthelot, *Compt. rend.* 42, 1111; *N. Ann. Chim. Phys.* 47, 297; 50, 369.)

Glycerin in contact with white cheese and many other animal substances, and chalk, yields alcohol; if no chalk is added, the glycerin remains for the most part unaltered, excepting under the circumstances above mentioned. (Berthelot.)

*Solubility of Lime in Aqueous Glycerin.* — Berthelot has determined the quantities of lime taken up by dilute solutions of glycerin of various strengths. In the following table, column I, gives the weight of glycerin in grammes contained in 100 cubic centimetres of the solution; column II, the weight of the lime contained in 100 c. c. of the liquid, when saturated with lime; column III, the ratio in which the lime and glycerin are mixed for a total of 100 pts.; and column IV, the same ratio, after deducting the quantity of lime dissolved by the pure water (100 c. c. water, dissolve 0.148 grm. of lime). The determinations were made at 5° C.

I. Glycerin.	II. Lime.	III.		IV.	
		Lime.	Glycerin.	Lime.	Glycerin.
10.00	0.370	3.6	96.4	2.2	97.8
5.00	0.240	4.6	95.4	1.8	98.2
2.86	0.196	6.4	93.6	1.7	98.3
2.50	0.192	7.1	92.9	1.7	98.3
2.60	0.186	8.5	91.5	1.8	98.2
1.00	0.165	14.2	85.8	1.7	98.3

From these results, Berthelot concludes that the quantities of lime dissolved in dilute solutions of glycerin, are to the quantities of glycerin in the same solutions in a constant ratio. (*N. Ann. Chim. Phys.* 46, 173.)

### Glyceric Acid. $C^3H^5O^3$ .

DEBUS. (1857.) *Phil. Mag.* [4] 13, 537. — Fully: *ibid.* 15, 196; *Ann. Pharm.* 106, 79. — Further: *Ann. Pharm.* 109, 227.

SOCOLOFF. *Petersb. Akad. Bull.* 16, 269; *Ann. Pharm.* 106, 95.

*Formation.* By the action of nitric acid on glycerin (Debus, Socoloff); also by the spontaneous decomposition of nitroglycerin. (De la Rue & Müller, *Ann. Pharm.* 109, 122).

*Preparation.* 1 pt. of glycerin is mixed in a glass cylinder with an equal bulk of water, and 1 pt. of nitric acid of sp. gr. 1.5 is introduced below it by means of a long-necked funnel (100 grms. glycerin, 100 grms. water, and 100 to 150 grms. red nitric acid are good proportions). The two layers of liquid gradually mix and assume a blue colour, and the oxidation of the glycerin proceeds, accompanied by a copious evolution of gas. If the liquid becomes too hot, the action must be moderated by external cooling. When the oxidation is completed, which takes 5 or 6 days, the strongly acid liquid is divided into small portions and evaporated at  $100^{\circ}$  to a syrupy consistence; the united residues are diluted with water and neutralized with chalk; and the resulting lime-salts are precipitated by strong alcohol. The liquid (which still contains one or two substances) is carefully separated from the precipitate; the latter is treated with warm water; and the solution filtered from the oxalate of lime is mixed with a quantity of milk of lime sufficient to produce alkaline reaction, whereupon the lime-salt of a peculiar acid is deposited. The liquid separated from this precipitate, freed from excess of lime by carbonic acid, and evaporated to the crystallizing point, yields glycerate of lime, which may be purified by recrystallization. (Debus.) — According to Socoloff, when glycerine is mixed with a large excess of nitric acid of sp. gr. 1.360, at ordinary temperatures, oxidation begins in a few hours, a large quantity of gas is evolved, and in a few days crystals of oxalic acid separate. When equal weights of glycerin (of sp. gr. 1.105) and nitric acid of sp. gr. 1.360 are mixed, no action takes place for several hours, but when once begun it becomes violent; it begins soon, if the mixture is heated; and if the vessel is removed from the source of heat, as soon as red fumes begin to escape, and then left to itself, an evolution of gas soon takes place, which may become violent if the quantity of the mixture exceeds 200 grms, and the nitrous vapours are soon replaced by a colourless gas. The liquid thus formed contains glyceric acid, the lime-salt of which may be obtained as above.

When the mother-liquor separated from the crystals of this lime-salt was mixed with carbonate of potash in quantity sufficient to precipitate the whole of the lime, and the alkaline filtrate neutralized with nitric acid and concentrated, the syrupy liquid decanted from the crystals of nitric which separated out, yielded needle-shaped crystals with a concentrated solution of bisulphite of soda: hence it probably contained a substance of the nature of an aldehyde. (Socoloff.)

By decomposing the lime-salt with a quantity of oxalic acid exactly sufficient to precipitate the lime, and evaporating the filtrate on the water-bath, free glyceric acid is obtained as a thick, yellow, non-crystallizing syrup, which, after being heated for some time to  $105^{\circ}$ , is converted into a soft, very tenacious, slightly brown mass having the composition of *glyceric anhydride*  $C^6H^4O^6$ , and changing at  $140^{\circ}$ , to a brownish mass like gum arabic, which absorbs water with avidity, and at a higher temperature gives off acid vapours, turns brown and burns with flame. (Debus.)

<i>Anhydride.</i>				<i>Debus.</i>			
6 C	.....	36	.... 40.90	.....	39.77	....	40.16
4 H	.....	4	.... 4.54	.....	5.24	....	5.35
6 O	.....	48	.... 54.56				
<hr/>							
$C^6H^4O^6$	.....	88	.... 100.00				

Isomeric with pyruvic acid (ix, 418). The difference between the analytical and calculated results is attributable to the difficulty of completely dehydrating the acid without further decomposing it.

Glyceric acid  $C^6H^6O^3$  is homologous with glyoxylic acid (xii, 506), and bears the same relation to glycerin  $C^6H^8O^6$  that acetic acid  $C^4H^4O^2$ , bears to alcohol  $C^4H^6O^2$ . (Debus.)

The aqueous solution of the acid has an agreeably sour taste dissolves iron and zinc with evolution of gas, decomposes carbonates, and coagulates milk. Potash added to a solution of iron in glyceric acid, precipitates only a part of the iron; the precipitation of copper from the sulphate by potash is likewise prevented by the presence of glyceric acid, the liquid yielding however a dark yellow-brown precipitate when boiled. (Debus.)

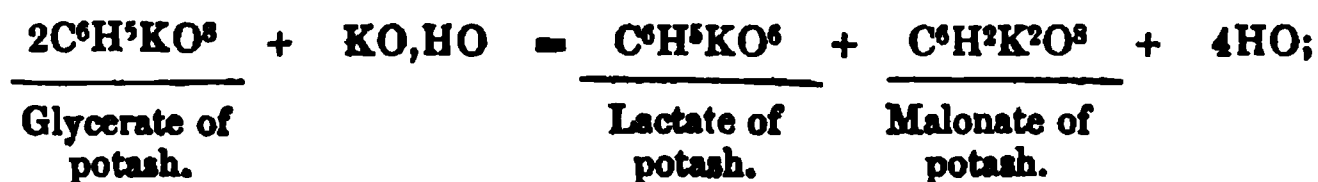
The basicity of glyceric acid is at present undetermined. The *glycerates* crystallize well. They are not reddened by ferrous sulphate, and are thereby distinguished from the salts of pyruvic acid.

*Glycerate of Ammonia.*  $C^6H^5(NH^4)O^3$ .—Obtained by decomposing the lime-salt with oxalate of ammonia, evaporating the filtrate to a syrup (replacing the small quantity of ammonia which escapes), and leaving it crystallize. Forms colourless radiating crystals, which are very deliquescent, melt at a gentle heat, and at higher temperatures give off ammonia and turn brown.

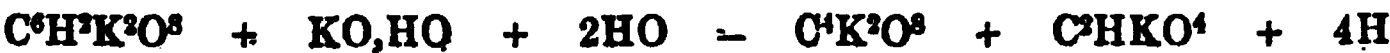
					Debus.
6 C	.....	36	...	29.26	..... 29.80
9 H	.....	9	...	7.31	..... 7.76
N	.....	14	...	11.40	
8 O	.....	64	...	52.03	
<hr/>					
$C^6H^5(NH^4)O^3$		123	...	100.00	

*Acid Glycerate of Potash.*  $C^6H^5KO^3, C^6H^5O^3$ .—By exactly neutralizing glyceric acid with carbonate of potash, mixing the solution with an equal quantity of glyceric acid, and evaporating at  $100^\circ$  to a syrup, this salt is obtained in small white crystals which give by analysis 15.8 p. c. potassium, agreeing exactly with the formula above given. This salt does not appear to contain any water that can be expelled without giving rise to further decomposition. (Debus.)

When 1 pt. of *neutral glycerate of potash* is mixed with 1 pt. of hydrate of potash dissolved in 2 pts. of water, and the liquid is boiled down, till a sample, after acidulation with acetic acid, gives a white precipitate with acetate of lead, the glyceric acid is found to be resolved into oxalic and lactic acids, the former being precipitated by acetate of lead from the acidulated liquid, while the latter remains dissolved. The glyceric acid is probably first resolved into lactic and malonic acids (p. 560):



and the malonic acid is further resolved into oxalic and formic acids:



From an experiment made by Atkinson, it appears that glycerate of potash under the influence of potash in a state of fusion is resolved into acetate and formiate of potash :



(Debus, *Ann. Pharm.* 109, 227.)

*Glycerate of Baryta.*  $\text{C}^6\text{H}^5\text{BaO}^8$ . — Separates from a hot solution of carbonate of baryta in aqueous glyceric acid, in large spherical aggregations of concentrically grouped laminæ. (Socoloff.)

					Socoloff.
6 C	.....	36.0	....	20.75	..... 20.58
5 H	.....	5.0	....	2.88	... .. 3.07
Ba	.....	68.6	....	39.48	..... 39.45
8 O	.....	64.0	....	39.89	..... 36.90
<hr/>					
$\text{C}^6\text{H}^5\text{BaO}^8$	....	173.6	....	100.00	..... 100.00

*Glycerate of Lime.*  $\text{C}^6\text{H}^5\text{CaO}^8 + 2\text{Aq}$ . — *Preparation* (p. 569). — Crystallizes in small white concentrically grouped crystals, frequently also in nodules composed of microscopic rhombic tables or prisms (Debus). The most distinct crystals are obtained by mixing a moderately concentrated aqueous solution of the salt with an equal volume of hot alcohol. They are monoclinometric (oblique prismatic) combinations,  $\infty \text{P} . \infty \text{P} . (\infty \text{P} \infty) . \infty \text{P} \infty$ , and have a micaceous lustre (Socoloff). They give off 12.15 p. c. (2 At.) water, slowly between  $110^\circ$  and  $120^\circ$ , more quickly between  $130^\circ$  and  $140^\circ$ , melting at the same time ; at  $160^\circ$  the salt does not give off more water, but begins to decompose. After being heated to between  $160^\circ$  and  $170^\circ$ , it forms a strongly tumefied mass, which has an empyreumatic odour and slight brownish colour, and absorbs water with rapidity from the air, being thereby converted into a brown glutinous liquid, which after a few days yields crystals of the original salt with 2 At. water, together with a brown greasy mass.

<i>Dried over oil of vitriol.</i>					Debus.	Socoloff.
6 C	.....	36	....	25.17	..... 25.18	..... 25.15
7 H	.....	7	....	4.89	..... 5.10	..... 5.02
Ca	.....	20	....	13.98	..... 14.00	..... 13.99
10 O	.....	80	....	55.96	..... 55.72	..... 55.84
<hr/>						
$\text{C}^6\text{H}^5\text{CaO}^8 + 2\text{Aq}$	.....	143	....	100.00	..... 100.00	..... 100.00

Glycerate of lime is easily soluble in water, insoluble in alcohol. The aqueous solution does not precipitate nitrate of silver, nitrate of lead, chloride of copper, or sesquichloride of iron ; with nitrate of silver at the boiling heat, it forms a black precipitate, and if ammonia is present, a specular deposit of silver.

An acid glycerate of lime does not appear to exist.

*Glycerate of Zinc.*  $C^6H^5ZnO^3 + Aq.$  — Crystallizes from a solution of carbonate of zinc in warm aqueous glyceric acid, in small colourless crystals, which give off their water 6·4 p. c. at 140°. (Debus.)

<i>Dried at 140°.</i>						Debus.
6 C	.....	36·0	....	26·16	.....	26·23
5 H	.....	5·0	....	3·63	.....	3·89
Zn	.....	32·6	....	23·69	.....	23·83
8 O	.....	64·0	....	46·52	.....	46·05
<hr/>						
C <sup>6</sup> H <sup>5</sup> ZnO <sup>3</sup>	.....	137·6	....	100·00	.....	100·00

*Glycerate of Lead.*— $C^6H^5PbO^3$ .—Prepared by adding pure and pulverized oxide of lead by small portions to dilute aqueous glyceric acid till the liquid retains but a slight acid reaction, then filtering quickly, and concentrating the filtrate, if necessary, at 100°. The lead-salt then separates after a while, in white hard crystalline crusts which are anhydrous. (Debus.)

<i>Dried over oil of vitriol</i>					Debus.
6 C	.....	36·0	....	17·24	..... 16·87
5 H	.....	5·0	....	2·39	..... 2·47
Pb	.....	103·7	....	49·71	..... 49·44
8 O	.....	64·0	....	30·66	..... 31·22
<hr/>					
C <sup>6</sup> H <sup>5</sup> PbO <sup>3</sup>	.....	208·7	....	100·00	..... 100·00

Glycerate of lead may be heated to 140° without alteration or loss of weight ; but at 165°, it turns brown and gives off empyreumatic vapours. It dissolves sparingly in cold water, with moderate facility in hot water : forming a neutral or slightly acid solution, which is rendered turbid by ammonia. (Debus.)

*Glycerate of Silver* is extremely unstable.

It does not appear possible to prepare a glycerate of ethyl. (Debus.)

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Page 492.

## Glycerides.

BERTHELOT & DE LUCA. *N. Ann. Chim. Phys.* 48, 304 ; abstr. *Ann. Pharm.* 101, 67 ; *Liebig & Kopp's Jahresber.* 1856, 598. — Further : *N. Ann. Chim. Phys.* 52, 433 ; abstr. *Compt. rend.* 45, 178, 244 ; *Jahresber.* 1857, 476.

*Action of Bromide of Phosphorus on Glycerin.* — The tribromide and pentabromide of phosphorus act in the same manner upon glycerin,



giving rise to products which may all be comprised in the general formula :



The names and formulæ of these compounds are given in the following table :

Monobromhydrin .....	$C^6H^7BrO^4$	=	$C^6H^8O^6$	+	HBr	-	2HO
Epibromhydrin .....	$C^6H^5BrO^2$	=	$C^6H^8O^6$	+	HBr	-	4HO
Bibromhydrin .....	$C^6H^6Br^2O^3$	=	$C^6H^8O^6$	+	2HBr	-	4HO
Hemibromhydrin .....	$C^{12}H^9BrO^4$	=	$2C^6H^8O^6$	+	HBr	-	8HO
Hexaglyceric bromhydrin ....	$C^{36}H^{27}BrO^{14}$	=	$6C^6H^8O^6$	+	HBr	-	22HO

Besides these compounds, there are formed several liquids which volatilize in vacuo at 200° or above, and appear to be bromhydrins ; also a brominated compound, volatile between 65° and 67° and containing 32.9 p. c. carbon, 5.4 hydrogen, and 51.1 bromine ; acrolein ; and a phosphoretted compound,  $C^{12}H^9Br^2P = 2C^6H^8BrO^3 + PH^3 - 4HO$ .

*Preparation of the Bromhydrins.* — 500 grammes of glycerin are added by small portions to between 500 and 600 grms. of liquid bromide of phosphorus, the liquid being cooled after each addition, and the mixture, after standing for 24 hours, is distilled into a well cooled receiver communicating with a vessel containing potash-ley, to absorb the acrolein vapours. As an additional precaution against the injurious effects of these vapours, the distillation and all the subsequent operations should be performed either in the open air, or under a chimney with a good draught.

The distillate, consisting of an upper watery layer and a lower liquid insoluble in water, may be freed from part of the acrolein by heating it in the water-bath. It is then mixed with potash in sufficient quantity to supersaturate the acid and destroy the acrolein, and the watery layer is separated from the lower liquid.

The watery liquid is then treated with ether, whereby an ethereal solution is obtained, which when quickly evaporated, leaves a residue chiefly consisting of the most volatile products of the reaction, together with *epibromhydrin*. The lower liquid, which is insoluble in water and requires to be treated for several hours with sticks of potash, consists chiefly of *epibromhydrin* and *bibromhydrin*. — The residue which remains in the retort after the distillation, is suspended in water, supersaturated with carbonate of potash, and shaken up with ether, and the filtered ethereal extracts are evaporated : they then leave a mixture of *bibromhydrin*, *monobromhydrin*, and several other substances.

To separate the individual substances contained in these several mixtures, the mixtures are subjected to repeated fractional distillation, and the portion which does not volatilize at 240° under the ordinary atmospheric pressure, is fractionally distilled under diminished pressure (about 10mm. of mercury). The distillate thus obtained between 120° and 160° consists chiefly of *bibromhydrin* ; between 160° and 200°, the compound  $C^{12}H^9Br^2P$  passes over together with *monobromhydrin*, and between 200° and 300°, syrupy liquids which cannot be further separated, but appear to be bromhydrins. In the retort there remains a thick syrup together with a black crystalline compound, which is hexaglyceric bromhydrin,  $C^{36}H^{27}BrO^{14}$ .



*Monobromhydrin.*  $\text{C}^6\text{H}^7\text{BrO}^4 = \text{C}^6\text{H}^8\text{O}^6 + \text{HBr} - 2\text{HO}$ . — This compound, which passes over in the distillation under diminished pressure at  $180^\circ$ , is a neutral oily liquid, soluble in ether and having a sharp aromatic taste. Heated to  $100^\circ$  with aqueous potash in closed vessels for 112 hours, it is converted into bromide of potassium and glycerin.

Berthelot & De Luca.					
6 C	.....	36	....	23.2	..... 22.0
7 H	.....	7	....	4.5	..... 3.6
Br	.....	80	....	51.6	..... 50.5
4 O	.....	32	....	20.7	..... 23.9
<hr/>					
$\text{C}^6\text{H}^7\text{BrO}^4$	.....	155	....	100.0	..... 100.0

The difference between the analytical and calculated results is owing to the great difficulty of separating the compound from the other substances with which it is mixed.

Monobromhydrin may be regarded as deriving from glycerin by the substitution of Cl for  $\text{HO}^2$ . The formula of glycerin may in fact be written in the form  $\text{C}^6\text{H}^5, \text{HO}^2, \text{HO}^2, \text{HO}^2$ , the replacement of 1 At.  $\text{HO}^2$  by Br giving monobromhydrin, a second such replacement giving bibromhydrin  $\text{C}^6\text{H}^5, \text{HO}^2, \text{Br}^2 = \text{C}^6\text{H}^6\text{Br}^2\text{O}^2$ , and the replacement of the third molecule of  $\text{HO}^2$  by Cl, giving terbromhydrin  $\text{C}^6\text{H}^5\text{Br}^3$ .

*Bibromhydrin.*  $\text{C}^6\text{H}^6\text{Br}^2\text{O}^2 = \text{C}^6\text{H}^8\text{O}^6 + 2\text{HBr} - 4\text{HO}$ , is the chief product of the action of bromide of phosphorus on glycerin. It is a neutral liquid of sp. gr. 2.11 at  $18^\circ$ , and boiling at  $219^\circ$ . It is soluble in ether, and has an ethereal odour.

Berthelot & De Luca.					
6 C	.....	36	....	16.5	..... 16.7
6 H	.....	6	....	2.7	..... 2.7
2 Br	.....	160	....	73.4	..... 73.4
2 O	.....	16	....	7.4	..... 7.2
<hr/>					
$\text{C}^6\text{H}^6\text{Br}^2\text{O}^2$	.....	218	....	100.0	..... 100.0

=  $\text{C}^6\text{H}^5, \text{HO}^2, \text{Cl}^2$ , glycerin with  $2\text{HO}^2$  replaced by  $\text{Br}^2$ .

Bibromhydrin heated for some time with aqueous potash is converted into bromide of potassium and glycerin ( $\text{C}^6\text{H}^6\text{Br}^2\text{O}^2 + 2\text{KHO}^2 = 2\text{KBr} + \text{C}^6\text{H}^8\text{O}^6$ ).

When gaseous ammonia is passed into pure bibromhydrin, the liquid becomes hot and coloured, and a mixture is formed of bromide of ammonium and an amorphous substance which is insoluble in water, ether, alcohol, and acetic acid, and has the composition  $\text{C}^{12}\text{H}^{12}\text{BrNO}^4$ :



but if the ammonia gas is passed into a solution of bibromhydrin in absolute alcohol, the products formed are bromide of ammonium and *hydrobromate of glyceramine*,  $\text{C}^6\text{H}^8\text{NO}^4$ . [For this reaction, Berthelot & De Luca give the equation :



the two sides of which do not agree, the right hand side containing  $\text{H}^2\text{O}^2$  more than the left.]—With pentabromide of phosphorus, it yields *terbromhydrin*,

$C^6H^5Br^3$ . — Heated to  $140^\circ$  with metallic tin, it is decomposed, with formation of bromide of tin, and a tin-compound not yet further examined, which is insoluble in water, but soluble in ether.

*Terbromhydrin*,  $C^6H^5Br^3$ . — Obtained by distilling bibromhydrin or epibromhydrin with pentabromide of phosphorus, treating the product with water, distilling, and collecting apart that which passes over between  $175^\circ$  and  $180^\circ$ . It is a heavy liquid, which fumes slightly in the air, is gradually decomposed by water, and when treated with moist oxide of silver, yields bromide of silver and glycerin.

Berthelot & De Luca.					
6 C	.....	86	....	12.8	..... 11.0
5 H	.....	5	....	1.8	..... 2.1
3 Br	.....	240	....	85.4	..... 86.2
<hr/>					
$C^6H^5Br^3$	.....	281	....	100.0	..... 99.3

Isomeric with Wurtz's *terbromide of allyl* (called by Berthelot & De Luca *isotribromhydrin*), and with *bibromide of bromopropylene*  $C^6H^5Br, Br^2$  (pp. 542, 553).

*Epibromhydrin*,  $C^6H^5BrO^2$ . — This compound is produced in considerable quantity in the action of the bromides of phosphorus on glycerin. It may be isolated by repeated fractional distillation, the portions which boil at or near  $138^\circ$  being each time collected apart. It is a mobile neutral liquid, soluble in ether, with an ethereal odour and pungent taste. Sp. gr. 1.615 at  $14^\circ$ . Boils at  $138^\circ$ . Vapour-density, by experiment, 5.78. This is considerably above the calculated value, probably because the density was taken at a temperature too near the boiling point, viz., at  $178^\circ$ , the compound decomposing rapidly at higher temperatures.

Berthelot & De Luca.					
6 C	.....	36	....	26.3	..... 25.8
5 H	.....	5	....	3.7	..... 3.3
Br	.....	80	....	58.4	..... 57.8 .... 58.4
2 O	.....	16	....	11.6	
<hr/>					
$C^6H^5BrO^2$	.....	137	....	100.0	

	Vol.	Density.
C-vapour	6	2.4960
H-gas	5	0.3465
Br-vapour	1	5.5440
O-gas	1	1.1093
<hr/>		
Vapour of Epibromhydrin	2	9.4958
	1	4.7979

Isomeric with bromide of propionyl  $C^6H^5O^2, Br$ . The formula is also that of monobromhydrin —  $2HO$ , or of bibromhydrin —  $HBr$ .

Epibromhydrin, heated with aqueous potash to  $100^\circ$  for 112 hours, saponifies, yielding bromide of potassium, glycerin, and a trace of matter

soluble in ether. — Moist oxide of silver decomposes it rapidly at 100°, forming bromide of silver and glycerin. — Distilled with pentabromide of phosphorus, it is partly converted into terbromhydrin, according to the equation :



while the rest undergoes more complete decomposition, yielding a black substance and a gaseous mixture, containing, in 100 volumes, 5.5 carbonic acid, 5.5 propylene, 11.0 hydrogen, and 78.0 carbonic oxide.

				Berthelot & De Luca.			
				<i>distilled.</i>		<i>not distilled.</i>	
12 C	.....	72	....	26.5	.....	25.6	.... 26.6
9 H	.....	9	....	3.3	.....	3.4	.... 3.1
2 Br	.....	160	....	58.8	.....	58.8	.... 59.1
P	.....	31	....	11.4	.....		.... 10.5
<hr/>							
C <sup>12</sup> H <sup>9</sup> Br <sup>2</sup> P	.....	272	....	100.0	.....		.... 99.3

This compound is exactly analogous in composition to bibromallylamine  $\text{C}^{12}\text{H}^9\text{Br}^2\text{N}$  (p. 549), the nitrogen in that compound being replaced by phosphorus. It contains the elements of 2 At. epibromhydrin and 1 At. phosphoretted hydrogen *minus* 4 At. water ( $2\text{C}^6\text{H}^5\text{BrO}^2 + \text{PH}^3 - 4\text{HO}$ ), and is probably formed by a secondary reaction.

*Hexaglyceric Bromhydrin.*  $\text{C}^{36}\text{H}^{27}\text{BrO}^4 = 6\text{C}^6\text{H}^5\text{O}^6 + \text{HBr} - 22\text{HO}$ . — This compound remains in the retort (p. 573) in the form of a black crystalline mass, impregnated with a syrupy liquid. It is purified by washing with cold ether : boiling ether dissolves it slightly.

				Berthelot & De Luca.			
36 C	.....	216	....	49.7	.....	50.0	
27 H	.....	27	....	6.2	.....	6.5	
Br	.....	80	....	18.4	.....	18.6	
4 O	.....	32	....	25.7	.....	24.9	
<hr/>				<hr/>			
$\text{C}^{36}\text{H}^{27}\text{BrO}^4$	.....	355	....	100.0	.....	100.0	

*Hemibromhydrin.* —  $\text{C}^{12}\text{H}^9\text{BrO}^4 = 2\text{C}^6\text{H}^5\text{O}^6 + \text{HBr} - 8\text{HO}$ . This and the two following compounds are likewise formed by the action of bromide of phosphorus on glycerin, but in much smaller quantity than those above described. Hemibromhydrin passes over in the fractional distillation between epibromhydrin and bibromhydrin, viz., at 200°. It is a neutral liquid, soluble in ether, and saponifiable by potash, yielding bromide of potassium, a substance analogous to or identical with glycerin, and a trace of matter soluble in ether. The analyses of this compound are said to agree nearly with the above formula [no analyses are given in Berthelot & De Luca's memoir], according to which it may be regarded as deriving from epibromhydrin, in the same manner as the latter from bibromhydrin, viz., by abstraction of half the hydrobromic acid :



and—



It is analogous in composition to iodhydrin (ix, 500).

*Bi-epibromhydrophosphoryl* or *Bibromallylphosphine*.  $C^{12}H^9Br^3P = PH(C^6H^4Br)^3$ . — This compound distils over, almost at the same temperature as monobromhydrin. The same body usually crystallizes spontaneously in the products which are non-volatile at  $240^\circ$ , when they have been purified by potash and ether before being distilled in vacuo. It is purified by recrystallization from boiling ether, and then forms white, shining prismatic crystals, volatile without decomposition, and sparingly soluble in ether. It is not sensibly attacked by aqueous potash at  $100^\circ$ , even after a considerable time.

## Chlorhydrins.

BERTHELOT & DE LUCA. See Memoirs cited at page 572.

These compounds are analogous to the bromhydrins. Three of them, viz., *monochlorhydrin*, *bichlorhydrin*, and *epichlorhydrin*, have been already described (ix, 498), as produced by the action of hydrochloric acid upon glycerin. They may also be obtained by treating glycerin with terchloride or pentachloride of phosphorus, the mode of preparation and separation being exactly similar to that of the bromhydrins. It is necessary however, to work with an excess of glycerin, to prevent the action from becoming too violent; the products are not very abundant.

*Terchlorhydrin*.  $C^6H^5Cl^3$ . — *Terchloride of Glyceryl*. — Produced by the action of pentachloride of phosphorus on bichlorhydrin :



It is a neutral liquid, much more stable than terbromhydrin; volatilizes at about  $155^\circ$ .

Berthelot & De Luca.					
6 C	.....	36.0	...	24.4	..... 24.0
5 H	.....	5.0	...	3.4	..... 3.4
3 Cl	.....	106.5	...	72.2	..... 72.0
<hr/>					
$C^6H^5Cl^3$	.....	147.5	...	100.0	..... 99.4

*Epibichlorhydrin*.  $C^6H^4Cl^3$ . — *Epidichlorhydrin*; *Bichloride of Glycerylene*. Produced in small quantity in the preparation of terchlorhydrin and bromobichlorhydrin; probably by a secondary reaction, inasmuch as it differs from bichlorhydrin,  $C^6H^6Cl^2O^2$ , by 2 At. HO, and from terchlorhydrin, by 1 At. HCl. It is isolated and purified by repeated fractional distillation.

It is a neutral liquid, volatile at about  $120^\circ$ . Treated with moist oxide of silver, at  $100^\circ$ , it slowly reproduces glycerin.

Berthelot & De Luca.					
6 C .....	36	...	32.4	.....	31.0
4 H .....	4	...	3.6	.....	3.6
2 Cl .....	71	...	64.0	.....	66.0
<hr/>					
C <sup>6</sup> H <sup>4</sup> Cl <sup>2</sup> .....	111	...	100.0	.....	100.6

*Bibromochlorhydrin.* C<sup>6</sup>H<sup>5</sup>Br<sup>2</sup>Cl. — *Chlorhydrodibromhydrin*; *Bibromochloride of Glyceryl*. — Produced by the action of pentachloride of phosphorus on bibromhydrin (p. 574). — Neutral liquid, volatile at about 200°. Treated with moist oxide of silver at 100°, it slowly reproduces glycerin.

Berthelot & De Luca.					
6 C .....	36	...	15.3	.....	16.0
5 H .....	5	...	2.1	.....	2.1
2 Br .....	160	...	67.7	.....	68.0
Cl .....	36.5	...	14.9	.....	14.0
<hr/>					
C <sup>6</sup> H <sup>5</sup> Br <sup>2</sup> Cl.....	237.5	...	100.0	.....	100.0

Isomeric with bibromide of chloropropylene.

*Bromobichlorhydrin.* C<sup>6</sup>H<sup>5</sup>BrCl<sup>2</sup>. — *Bromhydrodichlorhydrin*; *Bromobichloride of Glyceryl*. — Produced by the action of pentabromide of phosphorus on bichlorhydrin :

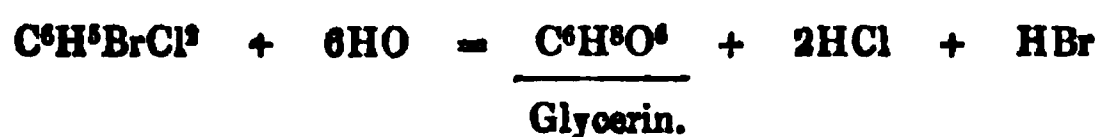


Neutral heavy liquid, volatile at about 176°.

Berthelot & De Luca.					
6 C .....	36	...	18.7	.....	17.9
5 H .....	5	...	2.6	.....	2.7
Br .....	80	...	37.0	.....	38.0
2 Cl .....	36.5	...	41.7	.....	40.9
<hr/>					
C <sup>6</sup> H <sup>5</sup> BrCl <sup>2</sup> .....	157.5	...	100.0	.....	99.5

Isomeric with bichloride of bromopropylene.

Treated with moist oxide of silver at 100°, it slowly regenerates glycerin; at the same time however, a small quantity of carbonic acid is formed by oxidation, and crystalline scales nearly insoluble in water, which appear to be propionate of silver.



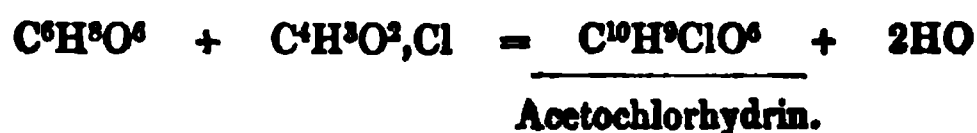
and—



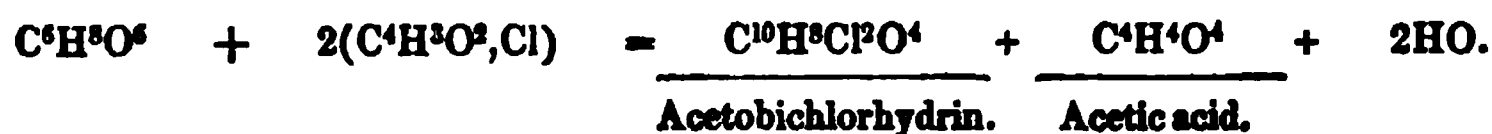
## Acetochlorhydrins.

BERTHELOT & DE LUCA. *N. Ann. Chim. Phys.* 52, 459.

*Formation and Preparation.* By the action of chloride of acetyl on glycerin. 250 grammes of glycerin are introduced into a tubulated retort surrounded by cold water, and chloride of acetyl is added by small portions, till a fresh addition no longer causes evolution of heat; the quantity of chloride of acetyl required is very large. When the reaction is finished, the liquid is distilled, the portion which passes over from 180° to about 260°, being collected apart; the distillate is shaken up first with water, then with an alkaline liquid, afterwards digested for a day with a mixture of chloride of calcium and quicklime, or fragments of potash, and then redistilled. The first portion, which is the most abundant and passes over at about 205°, contains chiefly *acetobichlorhydrin*, which may be separated and purified by repeated distillation. Afterwards at about 250°, *acetochlorhydrin* passes over, though in much smaller quantity than the preceding :



and—



*Acetochlorhydrin.*  $\text{C}^{10}\text{H}^9\text{ClO}^6 = \text{C}^6\text{H}^8\text{O}^6 + \text{C}^4\text{H}^4\text{O}^4 + \text{HCl} - 4\text{HO}$ . — Neutral colourless liquid, having the fresh ethereal odour of acetate of ethyl, but weaker. Volatile at about 250°.

Berthelot & De Luca.

10 C .....	60.0	....	39.3	
9 H .....	9.0	....	5.9	
Cl .....	35.5	....	23.3	..... 24.0
6 O .....	48.0	....	31.5	
<hr/>				
$\text{C}^{10}\text{H}^9\text{ClO}^6$ .....	152.2	...	100.0	

May be regarded as glycerin  $(\text{C}^6\text{H}^8)''', (\text{HO}^2)^3$ , in which 1 At.  $\text{HO}^2$  is replaced by peroxide of acetyl  $\text{C}^4\text{H}^3\text{O}^4$ , and another by Cl, viz., as  $(\text{C}^6\text{H}^8)''', \text{HO}^2, \text{C}^4\text{H}^3\text{O}^4, \text{Cl}$ .

*Acetobichlorhydrin.*  $\text{C}^{10}\text{H}^8\text{Cl}^2\text{O}^4 = \text{C}^6\text{H}^8\text{O}^6 + \text{C}^4\text{H}^4\text{O}^4 + 2\text{HCl} - 6\text{HO}$ . — This compound is likewise obtained by passing hydrochloric acid gas for two or three days, through a mixture of equal volumes of glycerin and glacial acetic acid heated to 100°; but this mode of preparation is not so good as that above given, because a large quantity of bichlorhydrin is formed at the same time (*comp.* ix, 498).

Limpid neutral oil, having the fresh ethereal odour of acetate of

ethyl. Boils and distils at  $250^{\circ}$ , without decomposition. Sparingly soluble in water.

Berthelot & De Luca.					
10 C	.....	60	...	35.1	..... 35.7
8 H	.....	8	...	4.7	..... 4.1
2 Cl	.....	71	...	41.5	..... 40.5 ... 41.6
4 O	.....	32	...	18.7	..... 19.7
<hr/>					
$C^{10}H^8Cl^2O^4$	...	171	...	100.0	..... 100.0

=  $(C^6H^5)'''C^4H^3O^4Cl^2$ . Isomeric with bichlorinated valeric acid, bichlorinated butyrate of ethyl, &c.

Treated with baryta-water at  $100^{\circ}$ , it is decomposed, yielding glycerin, together with chloride and acetate of barium. — Mixed in the cold with absolute alcohol and hydrochloric acid, it forms acetic ether.

*Biacetochlorhydrin.*  $C^{14}H^{11}ClO^8 = C^6H^8O^6 + 2C^4H^4O^4 + HCl - 6HO$ . — Produced by the action of chloride of acetyl on a mixture of equal volumes of glycerine and crystallizable acetic acid. The product is distilled, and the portion which passes over between  $230^{\circ}$  and  $260^{\circ}$ , is collected apart and submitted to fractional distillation.

Neutral liquid, having a faint odour, and boiling at about  $245^{\circ}$ . It is difficult to purify it from triacetin, which is formed at the same time; consequently the analysis gave rather too much carbon, and too little chlorine.

*Bromide of acetyl* acts upon glycerine in a similar manner to the chloride, producing analogous compounds.

*Acetochlorobromhydrin.*  $C^{10}H^8BrClO^4$ . — Obtained by treating glycerin with a mixture of bromide and chloride of acetyl in equal numbers of atoms. It is a neutral, limpid, colourless liquid, which becomes slightly coloured by exposure to light. It has a faint odour, recalling that of acetic ether and of bromide of ethylene. Boils at  $228^{\circ}$ , and distils without sensible decomposition.

Berthelot & De Luca.					
10 C	.....	60.0	...	27.8	..... 27.5
8 H	.....	8.0	...	3.7	..... 3.9
Br	.....	80.0	...	37.2	..... 36.0
Cl	.....	35.5	...	16.5	..... 16.5
4 O	.....	32.0	...	14.8	..... 16.1
<hr/>					
$C^{10}H^8BrClO^4$	...	215.5	...	100.0	..... 100.0

=  $(C^6H^5)'''C^4H^3O^4BrCl$ . — Isomeric with chlorobrominated valeric acid, chlorobrominated butyrate of methyl, &c.

### Glycerides of Polybasic Acids.

J. M. VAN BREMMELLEN. *J. pr. Chem.* 69, 84; abstr. *Jahresber.* 1856, p. 602; *Jahresber. d. Chem.* 1856, 602. Further: *Jahresber.* 1858, 434.

DESPLATS. *Compt. rend.* 49, 216.

*Succinin.*  $C^{14}H^{10}O^{10}$ . — Produced by heating together equal weights of glycerin and succinic acid at  $130^{\circ}$ . The two substances melt together

to a brown, syrupy mass, but no chemical combination takes place; but when they are heated for several hours to between 200° and 260°, water is given off, and finally also a small portion of glycerin. The residue is a hard black-brown mass, insoluble in water, alcohol, ether, and bisulphide of carbon.

	Dried at 160°.			van Bemmelen.	
14 C .....	84	....	48.27	.....	48.45
10 H .....	10	....	5.75	.....	5.79
10 O .....	80	....	45.98	.....	45.76
<hr/>					
C <sup>14</sup> H <sup>10</sup> O <sup>10</sup> .....	174	....	100.00	.....	100.00
<hr/>					
$= \left\{ \begin{array}{l} (\text{C}^6\text{H}^5)''' \\ (\text{C}^8\text{H}^4\text{O}^4)', \text{H} \end{array} \right\} \text{O}^6 = \text{C}^6\text{H}^8\text{O}^6 + \text{C}^8\text{H}^6\text{O}^8 - 4\text{HO}$					

Succinin dissolves slowly when boiled with water and alcohol; slowly also in alkalies in the cold, more quickly when heated. By continued boiling with oxide of lead, it is decomposed, yielding succinic acid and glycerin. (van Bemmelen.)

*Benzosuccinin.* C<sup>28</sup>H<sup>14</sup>O<sup>12</sup>. — Obtained by heating glycerin, succinic acid, and benzoic acid, in equal numbers of atoms to 200°, water and benzoic acid then escaping, and repeatedly heating the product to 200° with benzoic acid. The product is a viscid black-brown mass, which is decomposed by continued boiling with water and with alcohol, also by boiling with caustic potash, the solution in the latter case containing benzoic and succinic acid:

				van Bemmelen.	
28 C .....	168	....	60.43	.....	57.27
14 H .....	14	....	5.04	.....	5.42
12 O .....	96	....	34.53	.....	37.31
<hr/>					
C <sup>28</sup> H <sup>14</sup> O <sup>12</sup> .....	278	....	100.00	.....	100.00
<hr/>					
$= \left\{ \begin{array}{l} (\text{C}^6\text{H}^5)''' \\ (\text{C}^8\text{H}^4\text{O}^4)', \\ \text{C}^{14}\text{H}^2\text{O}^2 \end{array} \right\} \text{O}^6 = \text{C}^6\text{H}^8\text{O}^6 + \text{C}^8\text{H}^6\text{O}^8 + \text{C}^{14}\text{H}^6\text{O}^4 - 6\text{HO}$					

The deficiency of carbon and excess of hydrogen in the analysis show that the transformation of the glycerin was not quite complete.

*Glycero-succinic acid.* When a mixture of 1 At. glycerin and 1 At. succinic acid is heated to 160°, till it forms a homogeneous mass, a brown syrup is obtained, which dissolves readily in water and forms salts with bases. On triturating this syrup with oxide of lead under water, the uncombined succinic acid separates as succinate of lead, while *glycero-succinate of lead* remains in solution. The solution evaporated in vacuo leaves the salt in the form of a gummy, easily decomposable mass, somewhat soluble in alcohol. (van Bemmelen, *Jahresber. d. Chem.* 1858, 434.)

*Glyceroxalic acid* is produced when oxalic acid and glycerin are heated together, before the heat becomes strong enough to give rise to the production of formic acid (xii, 478). The lime-salt of this acid is soluble in water. (van Bemmelen.)

*Glyceromonotartaric acid*, C<sup>14</sup>H<sup>12</sup>O<sup>16</sup> = C<sup>8</sup>H<sup>6</sup>O<sup>12</sup> + C<sup>6</sup>H<sup>6</sup>O<sup>4</sup> - 2HO. — Obtained by heating a mixture of equal parts of tartaric acid and



glycerin to 100° for forty hours. The lime-salt is  $C^{14}H^{11}CaO^{12}$  (already analysed by Berzelius); and the baryta-salt,  $C^{14}H^{11}BaO^{12}$ . The magnesia, lead, copper, zinc, and silver salts are soluble in water, and are slowly, decomposed by water, more quickly with addition of lime or baryta, yielding glycerin and tartaric acid. (Desplats.)

*Glycerobitartronic acid.*  $C^{22}H^{16}O^{20} = 2C^6H^6O^{12} + C^6H^6O^6 - 4HO$ . — Obtained by heating to 100° for fifty hours a mixture of equal parts of tartaric acid and glycerin, in presence of a certain quantity of water. — The acid is bibasic. — Lime-salt,  $C^{22}H^{14}Ca^2O^{20}$ ; baryta-salt,  $C^{22}H^{14}Ba^2O^{20}$ . (Desplats.)

*Epiglycero-bitartaric acid.*  $C^{22}H^{14}O^{24} = 2C^6H^6O^{12} + C^6H^6O^6 - 6HO$ . — Obtained by heating to 140°, for a long time, a mixture of equal parts of glycerin and tartaric acid. — It is monobasic. Lime and baryta-salts,  $C^{22}H^{12}MO^{24}$ . (Desplats.)

*Glycerotertartaric acid.*  $C^{30}H^{22}O^{28} = 3C^6H^6O^{12} + C^6H^6O^6 - 4HO$ . — Produced by heating glycerobitartronic acid with 15 times its weight of tartaric acid, or 1 pt. of glycerin with 20 pts. of acid, and keeping the temperature at 140° for thirty hours. — The lime and baryta-salts are  $C^{30}H^{18}M^2O^{28}$ . (Desplats.)

*Citromonoglycerin.*  $C^{18}H^{10}O^{14}$ . — When citric acid and glycerin are heated together to 160° for 20 hours, in nearly equal numbers of atoms (the glycerin being in slight excess), water is given off, and there remains a hard, light, yellow, vitreous mass, which is citromonoglycerin. It is decomposed by alkalis and by oxide of lead, yielding citric acid and glycerin.

van Bemmelen.					
18 C	.....	108	...	47.0	..... 46.6
10 H	.....	10	...	4.3	..... 4.6
14 O	.....	112	...	48.7	..... 48.8
<hr/>					
$C^{18}H^{10}O^{14}$	.....	230	...	100.0	..... 100.0



*Citrobisglycerin.*  $C^{24}H^{12}O^{20} = C^{18}H^{10}O^{14}, C^6H^6O^6$ . — When citric acid is heated with a large excess of glycerin to 160° or 170° for several hours, there remains a yellow-brown residue, which appears to be a compound of 1 At. citromonoglycerin with 1 At. glycerin. It gives off glycerin when heated to 180° or 190°, and is reconverted into citric acid and glycerin by the action of alkalis or of oxide of lead. (van Bemmelen.)

van Bemmelen.					
24 C	.....	144	...	44.71	..... 44.82
18 H	.....	18	...	5.59	..... 5.47
20 O	.....	160	...	49.70	..... 49.71
<hr/>					
$C^{24}H^{12}O^{20}$	....	322	...	100.00	..... 100.00

$$= \left\{ \begin{matrix} (C^6H^5)_2 \\ H^2 \\ (C^{12}H^5O^8)''' \end{matrix} \right\} O^{12}, \text{ or a double molecule of glycerin, in which 3 At. H are replaced by citryl, } C^{12}H^5O^8. \text{ — Its formation is represented by the equation } 2C^6H^6O^6 + C^{12}H^{10}O^{14} = C^{24}H^{12}O^{20} + 6HO.$$

*Glycerocitric acid*, analogous to glycerosuccinic acid, is obtained by heating citric acid with glycerin to a temperature not sufficient to produce either of the preceding compounds. (van Bemmelen, *Jahresber. d. Chem.* 1858, 434.)

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Page 501.

*Nitroglycerin*.—This substance exhibits different properties according to the manner in which it is prepared.—Ordinary hydrated glycerin, added to a mixture of 3 pts. sulphuric and 1 pt. fuming nitric acid, is converted into a liquid which detonates violently under the hammer; but anhydrous glycerin treated in like manner, yields a non-explosive body which burns without noise. Both kinds of nitro-glycerin, when exposed to a mixture of solid carbonic acid and alcohol, become gummy and assume the appearance of fatty acids; and both decompose spontaneously, with evolution of red vapours. A sample of nitroglycerin which decomposed in this manner on exposure to summer sunshine, yielded crystals of oxalic acid, together with two liquids, the upper of which contained nitric acid, ammonia, oxalic acid, hydrocyanic acid, and other compounds not examined. (J. H. Gladstone, *Reports of the British Association*, 1856; *Jahresber. d. Chem.* 1857, 479.)

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*Glyceramine*.  $C^6H^9NO^4 = N.H^3, C^6H^7O^4$ . — (*Formation p.* 574).—It is likewise produced, in small quantity, by the action of ammonia on monochlorhydrin.—When separated from the hydrobromate by very strong potash-solution, it forms an oily liquid, easily soluble in water and in ether.—The *hydrchlorate* becomes moist on exposure to the air, blackens and decomposes when heated. Its alcoholic solution forms with bichloride of platinum, a double salt which separates in orange-coloured ranules. (Berthelot & De Luca, *Ann. Pharm.* 101, 74.)

	<i>Platinum-salt.</i>			<i>B. &amp; L.</i>	
6 C .....	36.0	...	12.1	.....	13.0
10 H .....	10.0	...	3.4	.....	2.9
N .....	14.0	...	4.8	.....	4.6
Pt .....	99.0	...	33.3	.....	32.7
3 Cl .....	106.5	...	35.6		
4 O .....	32.0	...	10.8		
<hr/>					
$C^6H^9NO^4, HCl, PtCl^2$ .....	297.5	...	100.0		

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## ADDITIONS TO VOL. XIII.

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Pages 123 and 137.

The salts of anisic and nitranisic acid have recently been more minutely examined by Engelhardt, (*Petersb Akad. Bull.* xvi, 289; *Ann. Pharm.* cviii, 240).

*Anisate of Potash*,  $C^{16}H^7KO^6$ , obtained by neutralising the acid with carbonate of potash, drying and recrystallization from 70 per cent. alcohol, forms thin nacreous laminæ which are anhydrous; after drying in the air, they contain 20·63 p. c. (Calculation 20·60 p. c.)

*Anisate of Soda*.  $C^{16}H^7NaO^6$ . — A solution of this salt in boiling alcohol yielded on cooling, transparent, shining, rhombic laminæ containing  $C^{16}H^7NO^6 + Aq$ , which at  $130^\circ$  gave off 5·11 p. c. (1 At.) water (calc. 4·92). When these laminæ were left for some time under the mother-liquor in an open vessel, they disappeared, and larger transparent crystals were formed, apparently belonging to the oblique prismatic (monoclinic) system, and giving off 13·36 p. c. (10 At.) water at  $130^\circ$  (calculation requiring 34·25 p. c.).

<i>Anhydrous-salt.</i>				Engelhardt.
$C^{16}H^7O^6$ .....	151	....	86·78	
Na .....	23	....	13·22	..... 13·10 to 13·6
<hr/>				
$C^{16}H^7NaO^6$ ....	174	....	100·00	

*Anisate of Baryta*,  $C^{16}H^7BaO^6$ , crystallizes by evaporation of its aqueous solution, in colourless, shining, rather thick, rhombic tables, which are anhydrous and sparingly soluble in water. The salt dried at  $160^\circ$  gave 31·09 p. c. barium (calculation : 31·20; Laurent's analysis (p. 126) gives 31·8 p. c. Ba).

*Anisate of Strontia*,  $C^{16}H^7SrO^6$ , + Aq, is precipitated by nitrate of strontia from a solution of anisate of ammonia, in shining laminæ, which

at  $140^{\circ}$  gave off 4.38 p. c. (1 At.) water (calculation : 4.41 p. c.). The dehydrated salt gave by analysis 22.22 p. c. strontium (calculation: 22.48 p. c.).

*Anisate of Lime.*  $C^{16}H^7CaO^6 + Aq.$  — The boiling aqueous acid saturated with carbonate of lime deposits on cooling, transparent, elongated laminæ, which at  $170^{\circ}$  give off 5.33 p. c. (1 At.) water (calculation 5.0 p. c.). The dehydrated salt gives 11.53 p. c. calcinm (calculation: 11.69 p. c.). The aqueous solution yields by slow evaporation short, transparent, flat prisms.

The anisates of baryta and lime did not yield bibasic salts, when treated in the manner by which Piria obtained bibasic salts from the corresponding salicylates (xii, 257).

*Anisate of Magnesia,*  $C^{16}H^7MgO^6 + 4Aq.$  is readily soluble in water and alcohol. From the alcoholic solution it crystallizes in flexible stellate needles which give off 16.93 p. c. (4 At.) water at  $00^{\circ}$  (calculation 16.41 p. c.). The anhydrous salt yielded 7.32 p. c. magnesium (calculation 7.36).

*Anisate of Lead. — a. Monobasic.*  $C^{16}H^7PbO^6 + HO.$  — Obtained by precipitating anisate of ammonia with neutral acetate of lead. White powder which dissolves in boiling water and crystallizes on cooling in thin nacreous laminæ, which give off their water (1 At.) between  $80^{\circ}$  and  $90^{\circ}$ , the salt then caking together and melting to a transparent, yellow, vitreous mass. The precipitated salt yielded 3.5 p. c.; the crystals 3.4 p. c. water (calculation : 3.41 p. c.). The dehydrated salt gave 39.19 p. c. of lead (calculation 39.32 p. c.).

*Bibasic.*  $C^{16}H^6Pb^2O^6 + Aq.$  — A boiling solution of the monobasic salt mixed with a solution of basic acetate of lead, forms a white heavy precipitate consisting of microscopic tables, which retain 1 At. water when dried over hydrate of potash. It gave off 2.48 p. c. water at  $140^{\circ}$ , and the dehydrated salt was found to contain 58.16 p. c. lead (calculation, 2.4 p. c. water and 58.03 lead).

*Anisate of Copper.*  $C^{16}H^6Cu^2O^6?$  — A solution of anisate of ammonia or anisate of soda forms with sulphate or acetate of copper a greenish blue precipitate which is a mixture of anisic acid with a basic salt. After extracting the free acid by means of ether, the residual salt dried at  $120^{\circ}$  gave by analysis a quantity of copper varying from 23.4 to 26.8 p. c. (the formula  $C^{16}H^6Cu^2O^6$  requires 25 per cent.). The precipitate obtained with anisate of soda and acetate of copper dissolves in boiling acetic acid, but the solution on cooling deposits anisic acid, the copper remaining dissolved.

**NITRANISATES. — Nitranisate of Potash.**  $C^{16}H^6XKO^6 + 2Aq.$  — Obtained by saturating nitranisic acid with carbonate of potash, evaporating dryness, and recrystallizing from boiling alcohol. Forms shining, elongated tablets, which give off 6.63 to 6.77 p. c. (2 At.) water at  $140^{\circ}$  (calculation 7.1 p. c.). The dehydrated salt  $C^{16}H^6XKO^6$  yielded by analysis 16.18 to 6.62 p. c. potassium. (Calculation 16.62 p. c.)

*Nitranisate of Soda*,  $C^{16}H^6XNaO^6 + 2HO$ , prepared in like manner, crystallizes from the hot aqueous solution in flat yellow needles (a), and from the hot alcoholic solution in slender yellow needles (b).

At 130°				Engelhardt.	
				(a)	(b)
$C^{16}H^6XO^6$	.....	196	.... 89.5	.....	
Na.....	.....	23	.... 10.5	.... 10.04	.... 10.42
<hr/>					
$C^{16}H^6XNaO^6$	....	219	.... 100.0	.....	

Crystallized.				Engelhardt.	
				(a)	(b)
$C^{16}H^6XNaO^6$	.....	219	.... 92.41		
2HO	.....	18	.... 7.59	..... 7.27	.... 7.42
<hr/>					
$C^{16}H^6XNaO^6 + 2Aq$	....	237	.... 100.00		

*Nitranisate of Baryta*.  $C^{16}H^6XBaO^6 + 4Aq$ . — Produced on adding nitrate of baryta to nitranisate of ammonia, as a white, flocculent precipitate, nearly insoluble in cold water, but much more soluble in boiling water: from the boiling solution it separates in flakes composed of microscopic needles. The air-dried salt gives off 11.7 p. c. (4 At.) water at 150°. (Calculation: 11.9 p. c.). — The dehydrated salt yields by analysis 25.74 p. c. barium. (Calculation: 25.89 p. c.).

*Nitranisate of Strontia*.  $C^{16}H^6XSrO^6 + 4Aq$ . — Resembles the baryta-salt. Gives off 12.5 p. c. (4 At.) water at 142°. (Calculation: 13.05 p. c.). The dehydrated salt yields by analysis 17.89 p. c. strontium. (Calculation: 18.22 p. c.).

*Nitranisate of Lime*,  $C^{16}H^6XCaO^6 + 4Aq$ , separates on mixing the solutions of nitranisate of soda and chloride of calcium, as a crystalline precipitate which when recrystallized from water yields flexible needles. The air-dried salt gives off 9.4 p. c. (4 At.) water at 150° (calculation: 10.8 p. c.); and the dried salt yields 9.19 p. c. calcium. (Calculation: 9.25 p. c.).

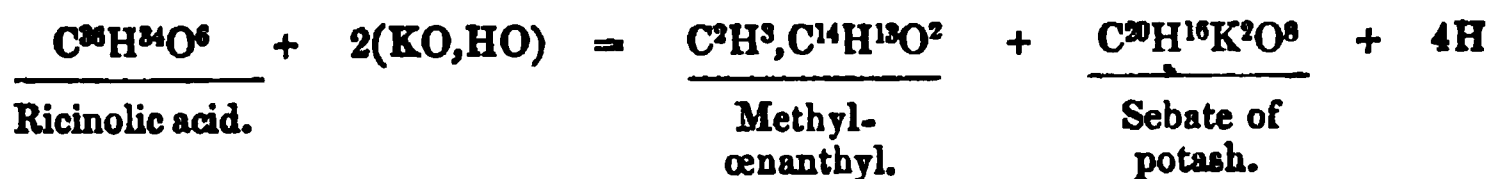
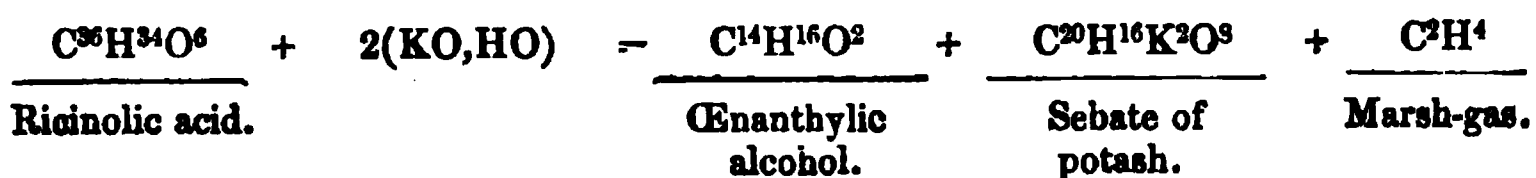
*Nitranisate of Lead*,  $C^{16}H^6XPbO^6$ , crystallizes from water in anhydrous needles which explode with violence at a red heat. After the explosion there was left 33 p. c. of lead, the calculated quantity being 34.63 p. c.

*Sulphanisic Acid*. — The normal baryta-salt of this acid, dried at 180° was found by Engelhardt to contain 37.08 p. c. barium, which is the same as the quantity found by Zervas (xiii, 129). When a portion of this salt was completely decomposed by sulphuric acid, an equal quantity of the undecomposed salt then added, and the mixture evaporated, a white granular mass was obtained, which yielded by analysis 30.1 to 30.7 p. c. barium, agreeing very nearly with the composition of the *sesquibasic* salt  $C^{16}H^6Ba^2O^6, 2SO^3 + C^{16}H^7BaO^6, 2SO^3$  (corresponding to the *sesquibasic* sulphosalicylate analysed by Mendius, xii, 277), which requires 30.8 p. c. barium.

Nitranisic acid is completely decomposed by the action of anhydrous sulphuric acid. (Engelhardt.)

Page 183.

*Caprylic Alcohol.* — Städeler (*J. pr. Chem.* 72, 241), maintains that the chief products of the distillation of castor-oil-soap (ricinolate of potash or soda) with excess of the alkali, are œnanthyl-alcohol and methyl-œnanthyl:



According to Dachauer, on the contrary (*Ann. Pharm.* 106, 270), the products of the distillation are methyl-œnanthyl and caprylic alcohol,  $\text{C}^{16}\text{H}^{18}\text{O}^2$ , the formation of the latter differing from that of the former only by the elimination of two atoms of hydrogen instead of four (p. 184). (It does not appear that Städeler actually observed the elimination of marsh-gas).

*Chloride of Capryl.* — On submitting the portion of the liquid, which in the distillation just mentioned, passed over between  $174^\circ$  and  $178^\circ$ , to the action of pentachloride of phosphorus (without previously treating it with bisulphite of soda to separate the methyl-œnanthyl) washing the resulting distillate with water, and distilling between  $171^\circ$  and  $175^\circ$ , a liquid was obtained, having the composition of chloride of capryl, as will be seen by comparing the analytical numbers with the calculation according to the formulæ  $\text{C}^{16}\text{H}^{17}\text{Cl}$  and  $\text{C}^{14}\text{H}^{15}\text{Cl}$ .

Calculation.				Dachauer.			
16 C	96.0	....	64.6	14 C	84.0	....	62.5
17 H	17.0	....	11.5	15 H	15.0	....	11.2
Cl	35.5	....	23.9	Cl	35.5	....	26.3
<hr/>				<hr/>			
$\text{C}^{16}\text{H}^{17}\text{Cl}$	148.5	....	100.0	$\text{C}^{14}\text{H}^{15}\text{Cl}$	134.5	....	100.0
							99.6

*Acetate of Capryl.*  $\text{C}^{20}\text{H}^{20}\text{O}^4 = \text{C}^4\text{H}^3(\text{C}^{16}\text{H}^{17})\text{O}^4$ . — Caprylic alcohol, freed from methyl-œnanthyl by treatment with bisulphite of soda, dissolves sodium in large quantity; and the resulting thick yellow mass, treated with chloride of acetyl, becomes heated, deposits chloride of sodium, and when water is poured upon it, is converted into a mobile liquid, which, after being dehydrated by repeated rectification, boiled constantly between  $191^\circ$  and  $192^\circ$ .

\* The numbers given in Dachauer's memoir are 64.1 C, 11.5 H, and 23.9 Cl, together making 100: there is, however, an error in the calculation. According to the atomic weight of chlorine which he adopts (36) his analysis would give 24.3 p. c. of chlorine, not 23.9. (W.)

Calculation.				Dachauer.	
20 C	.....	120	....	69.7	..... 70.0
20 H	.....	20	....	11.6	..... 11.9
4 O	.....	32	....	18.7	..... 18.1
<hr/>				<hr/>	
$C^4H^3(C^{16}H^{17})O^4$	.....	172	....	100.0	..... 100.0

The formula of acetate of œnanthyl  $C^{19}H^{19}O^4$  requires 68.4 C, 11.4 H, and 20.2 O.

*Chloride of Caprylene.*  $C^{16}H^{16}Cl^2$ .—Prepared: 1. By passing chlorine gas for a short time into water on which caprylene floats, drying the product, and distilling. A considerable quantity of undecomposed caprylene passes over at first; then the boiling point remains for a long time between  $190^\circ$  and  $200^\circ$ ; and of this product the greater portion, after repeated distillation, passes over between  $197^\circ$  and  $200^\circ$ .—By distilling methyl-œnanthyl ( $C^{16}H^{16}O^3$ ) with pentachloride of phosphorus, decomposing the distillate with water, and redistilling the insoluble oil. The greater part then passes over between  $190^\circ$  and  $200^\circ$ , which is about the boiling point of the product obtained by the first method.\*

				Dachauer.	
				(1)	(2)
16 C	.....	96	....	52.5	
16 H	.....	16	....	8.7	
2 Cl	.....	71	....	38.8	..... 39.4 .... 38.9 <sup>(a)</sup>
<hr/>				<hr/>	
$C^{16}H^{16}Cl^2$	....	183	....	100.0	

(a) The details of these determinations are not given.

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\* The isomeric compounds obtained by the action of chlorine on the hydrocarbons  $C^mH^m$ , and by that of pentachloride of phosphorus on the aldehydes, generally exhibit different boiling points: thus  $C^4H^4Cl^2$ , ordinary Dutch liquid, boils at  $82.5^\circ$ ; but the isomeric compound prepared by treating acetic aldehyde with pentachloride of phosphorus boils at  $60^\circ$ . (Geuther, *Ann. Pharm.* 106, 266.)

END OF VOL. XIII.

# REPORT

OF

## THE TWELFTH ANNIVERSARY MEETING

OF THE

### CAVENDISH SOCIETY.

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THE Anniversary Meeting of the Cavendish Society for the year 1859, was held at the rooms of the Chemical Society, in Burlington House, on Tuesday, the 1st of March, at three o'clock in the afternoon.

The Chair was taken by THOMAS GRAHAM, Esq., F.R.S., PRESIDENT, who called upon the Secretary to read

#### THE REPORT OF THE COUNCIL.

"In reporting the results of their proceedings to the Members, the Council have to state that two thick volumes have been added to the Works of the Cavendish Society since the last Anniversary meeting. These consist of the twelfth volume of GMELIN's 'Hand-book of Chemistry,' which has been supplied as a second book to those members who have subscribed for the year 1856; and the third and concluding volume of BISCHOF's 'Elements of Chemical and Physical Geology,' which is being issued as a book for 1858. The Council regret that they have not hitherto been able to supply more than one book for each of the years 1857 and 1858, and they feel it necessary to explain the circumstances which have led to this result.

"For several years past the Council have been seeking for works suitable for the Cavendish Society, and although many have from time to time been suggested, yet none of them has been found, after a careful consideration, to be such as the Council could feel justified in adopting, so that much difficulty has been experienced in providing suitable matter to keep up a full and regular supply of books to the members. This circumstance, probably, has tended to retard the payment of subscriptions; but independently of this, there has, during the last five or six years, been an evident falling off in the amount of support afforded to the Society; and with a diminished income the Council have felt it incumbent upon them, not only to be cautious in incurring liabilities, but also to endeavour to make the books supplied for each year bear some relation to the aggregate amount of the subscriptions paid for the same periods. Thus, for the years 1857 and 1858 the subscriptions which, up to the present time, have been paid, have not more than met the expenses involved in producing the two books already issued for those years, and the Preparation of other volumes for the same years must depend upon the means placed at the disposal of the Council, who, in accordance with the constitution of the Society, can only apply the funds provided by the subscribing Members.



"In the last Annual Report the Council referred to ROSE's 'Analytical Chemistry' as a work for the production of which in English they had made arrangements which appeared to be very satisfactory; and the first volume, edited by Mr. T. H. Henry, was then proposed to be made a second book for 1857. The Council have since been induced to alter this arrangement. They have been made aware by the author that a new edition of the work, in French, had been undertaken by him, and further, that the French edition would shortly be followed by a new and improved edition in German; they consequently thought it very undesirable to reproduce the work in English at the present time, and have, therefore, abandoned the undertaking.

"The Council have received the following communication from some of the members who were present at the meeting of the British Association at Leeds:—

" 'The undersigned Members of the Cavendish Society present at the meeting of the British Association in Leeds, beg respectfully to suggest to the Council of that Society the desirability of furnishing to the English Chemists an annual abstract of papers on Chemical Science published during the year.

" 'The existence of LIEBIG and KOPP's "Annual Report on the progress of Chemistry and the Allied Sciences," appears to us to offer a favourable basis for an arrangement by which such a desideratum might be supplied simultaneously in the German and English Languages. Signed, W. Vernon Harcourt, Robert Angus Smith, James Young, John Thom, William Odling, Robert Warrington, C. H. B. Hambly, H. C. Sorby, William Sykes Ward, Richard Reynolds, William Huggon, Thomas Harvey, J. H. Gilbert, W. J. Russell.'

"In connexion with this communication, it has been further suggested by one of the memorialists, Dr. R. Angus Smith, that works on the following subjects are much wanted by English Chemists, and might be suitably undertaken by the Cavendish Society:—

- " '1. A Repertorium of Chemical Literature.
- " '2. A Collection of Chemical Tables.
- " '3. A History of Chemistry.
- " '4. A History of the Arts in connexion with Chemistry.
- " '5. A Dictionary of Analyses, illustrating the Physical History, Geology, Mines, and Manufactures of England.
- " '6. A Dictionary of Analyses, the foundations of Scientific Chemistry.
- " '7. A reprint of the more remarkable documents of all times which have formed great eras in Chemical Science, or have served as germs of great truths in the Science.'

"These suggestions will be duly considered by the Council, but with reference to several of the subjects named, there appear to be difficulties in the way of obtaining competent authors to undertake them.

"The only work which the Council now have in hand, or to which they are committed, is the great work of Leopold Gmelin, with which the rise and progress of the Cavendish Society is so intimately associated. To the completion of this work the Society must hold itself pledged, and the Council have reason to believe, from communications which have been made to them, that they will best consult the wishes of the members by finishing this work before any other important undertaking is entered upon. The Council are fortunate in having the services of an editor who steadily

proceeds with the task he has undertaken, and who fully keeps pace with the production of the work in German. The thirteenth volume of the English translation is now in progress, and will be out in the course of a few months as a book for 1859; there will then be one more volume of the German edition to appear, which, with the new matter introduced by Mr. Watts in his translation, will make two, or at most, three volumes, of the size usually produced by this Society. It will be necessary to have a copious index to the whole work, and this will probably occupy an entire volume. Three or four volumes, in addition to the volume now in course of preparation, will, therefore, bring this great encyclopædia of chemical knowledge to a conclusion. With its introduction to English readers the mission of the Cavendish Society commenced, it has afforded a continued supply of matter, the appearance of which from year to year has been looked for with solicitude, and accompanied with expressions of satisfaction, which have served to indicate how greatly the success of the Society has been due to its influence; and when it shall be brought to a conclusion it will obviously be difficult to find another work so generally acceptable to the Members. Succeeding Councils will have to direct their attention to this subject, and to consider how far it will be practicable to maintain the Society in an active and efficient state, when the work for which it was chiefly called into existence, and which has hitherto formed the principal centre of union, shall have been accomplished.

“In forming a decision, it will be necessary to bear in mind, that for the efficient maintenance of the Society, with means for producing two volumes for each year, such as those usually produced by the Society, there must be about a thousand annual subscribers. This has been the average number of members who subscribed to the Society for the first five years of its existence, from 1848 to 1852, while for the three years extending from 1852 to 1855, the average number has been about seven hundred, and for the succeeding three years the contributing members have not exceeded five hundred; but the Council expect many subscriptions in arrear to be yet paid for the last three years.

“With the view of promoting the accession of new members, the Council have made arrangements for supplying those of the back volumes of GMELIN'S ‘Chemistry’ which still remain on hand, without the other works of the Society, as will be seen by reference to the statement appended to this report. All the copies of the first volume of Gmelin, treating of physics, have been disposed of, but there are several sets on hand of the ‘Inorganic Chemistry,’ from Vol. II to Vol. VI, inclusive, and of all the volumes treating of Organic Chemistry.

“In conclusion, the Council would submit to the Members that the interests of the Society demand, at the present time, their active co-operation. It is by paying up their back subscriptions, and by obtaining new subscribers, that the Members will render the most efficient aid to the Council, and thus enable them to complete, if not to extend the contributions to English scientific literature, which have been undertaken by the Cavendish Society.

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**STATEMENT of the RECEIPTS and EXPENDITURE of the CAVENDISH SOCIETY,  
from the 1st of March, 1858, to the 28th of February, 1859.**

RECEIPTS.		EXPENDITURE.	
	£ s. d.		£ s. d.
Balance from previous year	.. .. 200 14 10	Stationery and Petty Cash Expenditure	17 16 2
2 Subscriptions for 1848	.. .. 1 1 0	Insurance.. .. ..	2 4 0
1 Ditto 1853	.. .. 1 1 0	Collector's Commission .. ..	8 13 0
3 Ditto 1854	.. .. 3 3 0	Secretary, to 1st March, 1858 .. ..	35 0 0
8 Ditto 1855	.. .. 8 8 0	Agent for Distribution of Books, to 1st	
26 Ditto 1856	.. .. 27 6 0	March, 1858 .. .. ..	40 0 0
59 Ditto 1857	.. .. 61 19 0	Editorial expenses .. .. ..	284 10 0
141 Ditto 1858	.. .. 148 1 0	Paper .. .. ..	100 0 0
55 Ditto 1859	.. .. 57 15 0	Binding, wrapping, &c. .. ..	47 15 5
Subscriptions from America, less Agency	55 11 6		
12 Sets of Gmelin's 'Inorganic Chemistry'	25 4 0		
Sale of other Books .. ..	110 11 0	Balance in hand .. ..	164 16 9
	<u>£700 15 4</u>		<u>£700 15 4</u>

We have examined the above statement, and find it correct.

March 1, 1859.

CHAS. HEISCH.  
NEVIL STORY MASKELYNE.

It was resolved—

“That the Report just read be received, approved, and adopted.”

The Meeting then proceeded to the election of Officers for the ensuing year, and the following Gentlemen were declared to have been duly elected:—

**President.**

THOMAS GRAHAM, F.R.S.

**Vice-Presidents.**

PROFESSOR BRANDE, F.R.S.

DUKE OF DEVONSHIRE, F.R.S.

WALTER CRUM, F.R.S.

JOHN DAVY, M.D., F.R.S.

CHARLES G. B. DAUBENY, M.D., F.R.S.

MICHAEL FARADAY, D.C.L., F.R.S.

JOHN GRAHAM, F.C.S.

A. W. HOFMANN, Ph. D., LL.D.,  
F.R.S.

HENRY BEAUMONT LEESON, M.D.,  
F.R.S.

W. A. MILLER, M.D., F.R.S.

JOHN STENHOUSE, LL.D., F.R.S.

COLONEL PHILIP YORKE, F.R.S.

**Council.**

REV. J. BARLOW, F.R.S.

G. B. BUCKTON, F.R.S.

GEORGE BUSK, F.R.S.

DUGALD CAMPBELL, F.C.S.

P. J. CHABOT, M.A., F.R.A.S., F.C.S.

WARREN DE LA RUE, Ph.D., F.R.S.

W. FERGUSON, Esq.

E. FRANKLAND, Ph.D., F.R.S.

J. H. GILBERT, Ph.D., F.C.S.

CHARLES HEISCH, F.C.S.

N. S. MASKELYNE, F.C.S.

WILLIAM ODLING, M.B., F.C.S.

TRENHAM REEKS, Esq.

ALFRED SMEE, F.R.S.

R. D. THOMSON, M.D., F.R.S.

A. W. WILLIAMSON, Ph.D., F.R.S.

**Treasurer.**

GEORGE DIXON LONGSTAFF, M.D., 9, Upper Thames Street.

**Secretary.**

THEOPHILUS REDWOOD, Ph. D., 19, Montague Street, Russell Square,  
and 17, Bloomsbury Square.

**Collector.**

MR. THOMAS WEST, Burlington House, Piccadilly.

Agent for the Distribution of Books, &c.

MR. HARRISON, 59, Pall Mall.

It was resolved—

“That MESSRS. F. CLAUDET, JUN., DANIEL HANBURY,  
and DENHAM SMITH, be appointed Auditors for the ensuing  
year.”

The following Resolutions were unanimously adopted:—

“That the thanks of the Meeting be given to the PRE-  
SIDENT, TREASURER, and COUNCIL, for their services to the  
Society.”

“That the thanks of the Meeting be given to the HONORARY  
LOCAL SECRETARIES for their services to the Society.”

“That the thanks of the Meeting be given to the CHEMICAL  
SOCIETY for the use of their rooms.”

The Meeting was then adjourned.

THEOPHILUS REDWOOD, SECRETARY,  
19, Montague Street, Russell Square,  
and 17, Bloomsbury Square.

MARCH, 1859.

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